# THE THEORY OF THE VIBRATIONS AND THE RAMAN SPECTRUM OF THE DIAMOND LATTICE.

Thesis submitted by

Helen M. J. Smith, M.A.,

(University of Edinburgh)

for the degree of

Doctor of Philosophy.

EDINBURGH, MAY 1947.

CONTENTS.

INTRODUCTION.

The crystal structure of diamond was first determined by Bragg in 1913 from X-ray photographs: the carbon atoms are arranged at the apices and median points of inter-linked tetrahedra. Born (1914) derived expressions for the three elastic constants of diamond in terms of two force constants related to the valency bonds between neighbouring atoms. But, at that time the only experimental data available were the compressibility and the Debye characteristic temperature $\Theta$, and precise determination of the valence force constants was not possible. Meanwhile, investigation of the optical properties of diamond had produced evidence for the existence of two distinct types, one with an absorption band at $8\mu$ in the infra-red, the other transparent at this point. Robertson, Fox & Martin (1934) took up this problem and found that absorption in the infra-red is associated with absorption in the ultra-violet; diamonds transparent at $8\mu$ transmit much further into the ultra-violet. Both types of diamond have Bragg's tetrahedral structure, the same refractive index, specific gravity, dielectric constant, and electron diffraction. Their infra-red spectra are identical up to $7\mu$, and the frequency shift of the principal Raman line is the same. The derivation of the elastic constants was again considered by Nagendra Nath (1934).

He extended the theory to include central forces between second neighbours in the lattice. He also suggested that the frequency shift of the principal Raman line corresponds to the relative vibration of the two carbon atoms in the unit cell, along the line joining their nuclei.

Raman and his collaborators have recently (1941) put forward a new theory of lattice dynamics according to which the vibrational spectrum of a crystal consists of a few discrete lines. This is in direct contradiction to the quasi-continuous vibrational spectrum predicted by classical or quantum mechanics. On this new theory there are eight fundamental frequencies of vibration for diamond; the values of these frequencies are deduced from the observed specific heat, ultra-violet absorption, and Raman spectrum, which, it is claimed, cannot be explained by "orthodox" lattice dynamics. Now X-ray analysis determines the position of the nuclei in the lattice but gives no information about the electronic configurations so that if the two types of diamond were to differ in these configurations one would expect the dissimilarity in optical properties which, in fact, is observed. Raman (1944) has suggested that there are, not two, but four types of diamond, two with tetrahedral symmetry and two with octahedral symmetry, depending on the electronic configurations, but the attempts of his school to explain the observed infra-red spectra on the basis of their new lattice theory have been, up to now, unsuccessful.

Bhagavantam (1944) has developed a new method of measuring directly the elastic constants of crystals and has published results for diamond. This makes it possible for the first time to determine the force constants between the atoms in the lattice. The whole problem has therefore been reconsidered here on the lines of a general theory developed by Born (1942) assuming arbitrary forces between first neighbour atoms and central forces between second neighbour atoms. The values of the force constants are obtained from the measured elastic constants and the frequency shift of the principal Raman line. One can then derive approximations to the quasi-continuous vibrational spectrum of diamond and calculate the specific heat and Debye's characteristic temperature $\Theta$. Comparison with the observed specific heat shows that first neighbour forces alone are not sufficient to account for the experimental results but the addition of second neighbour central forces produces satisfactory agreement. The second-order Raman spectrum, first observed by Krishnan in 1944, can be calculated from the vibrational spectrum. The range and the positions of the maxima are obtained from theory without any arbitrary assumptions whatever, depending only on the measured constants. To explain the relative intensities of the parts of the spectrum it is necessary to postulate certain relations between coupling constants. These relations form the basis for further investigation of the possible differences between the electronic configurations in the two types of diamond. It is evident that Raman's claim, that lattice dynamics is unable to explain the Raman spectrum of diamond, is unfounded.

# PART I.

## THE THEORY OF THE VIBRATIONS OF THE DIAMOND LATTICE.

### 1. THEORETICAL BASIS.

This section summarises briefly results already obtained by Born (1942) and Born & Begbie (1947).

(a) Equations of motion of a crystal lattice.

The lattice cell is described by three elementary vectors $\underline{a}_1, \underline{a}_2, \underline{a}_3$. Then the position vector of the particle at the vertex of any cell is

(1.1) $$\underline{r}^{l} = l^1\underline{a}_1 + l^2\underline{a}_2 + l^3\underline{a}_3$$

where $l^1$, $l^2$, $l^3$ are integers.

If there are s particles in the unit cell with masses $m_k$ $(k = 1,2,..,s)$ and $\underline{r}_k$ is the position vector of the kth particle from the cell vertex, then

(1.2) $$\underline{r}\binom{l}{k} = \underline{r}^{l} + \underline{r}_k$$

defines the position of the particle $\binom{l}{k}$ in equilibrium. The rectangular components of $\underline{r}\binom{l}{k}$ are $x_\alpha\binom{l}{k}$, $(\alpha = 1,2,3)$.

Now consider small arbitrary displacements $\underline{u}\binom{l}{k}$ of the particles from equilibrium. The potential energy $\Phi$ of the deformed lattice can be expanded in powers of the rectangular components $u_\alpha\binom{l}{k}$ $(\alpha = 1,2,3)$ of $\underline{u}\binom{l}{k}$. The linear terms vanish in equilibrium and the second-order terms are

$$(1.3)\qquad \Phi_2 = \frac{1}{2}\sum_{lk}\sum_{l'k'}\sum_{\alpha\beta}\Phi_{\alpha\beta}\begin{pmatrix} l\,l' \\ k\,k' \end{pmatrix} u_\alpha\begin{pmatrix} l \\ k \end{pmatrix} u_\beta\begin{pmatrix} l' \\ k' \end{pmatrix}$$

$$(\alpha, \beta = 1, 2, 3)$$

where

$$(1.4)\qquad \Phi_{\alpha\beta}\begin{pmatrix} l\,l' \\ k\,k' \end{pmatrix} = \left[\frac{\partial^2 \Phi}{\partial x_\alpha\begin{pmatrix} l \\ k \end{pmatrix}\partial x_\beta\begin{pmatrix} l' \\ k' \end{pmatrix}}\right]_0 \;;$$

these second derivatives in equilibrium depend only on the difference of cell indices $(l-l')$, and satisfy the condition

$$(1.5)\qquad \Phi_{\alpha\beta}\begin{pmatrix} l \\ k\,k' \end{pmatrix} = \Phi_{\beta\alpha}\begin{pmatrix} -l \\ k'\,k \end{pmatrix} \;.$$

The equation of motion of a particle of type k, mass $m_k$, is then

$$(1.6)\qquad m_k \ddot{u}_\alpha\begin{pmatrix} l \\ k \end{pmatrix} + \sum_{l'k'}\sum_{\beta}\Phi_{\alpha\beta}\begin{pmatrix} l-l' \\ k\,k' \end{pmatrix} u_\beta\begin{pmatrix} l' \\ k' \end{pmatrix} = 0 \;.$$

Introduce a "reduced" displacement vector

$$(1.7)\qquad \underline{v}\begin{pmatrix} l \\ k \end{pmatrix} = \sqrt{m_k}\cdot \underline{u}\begin{pmatrix} l \\ k \end{pmatrix} \,,$$

and define the elements of the dynamical matrix of the lattice as

$$(1.8)\qquad D_{\alpha\beta}\begin{pmatrix} l-l' \\ k\,k' \end{pmatrix} = \frac{1}{\sqrt{m_k m_{k'}}}\,\Phi_{\alpha\beta}\begin{pmatrix} l-l' \\ k\,k' \end{pmatrix} \;.$$

Then (1.6) becomes

$$(1.9)\qquad \ddot{v}_\alpha\begin{pmatrix} l \\ k \end{pmatrix} + \sum_{l'k'}\sum_{\beta} D_{\alpha\beta}\begin{pmatrix} l-l' \\ k\,k' \end{pmatrix} v_\beta\begin{pmatrix} l' \\ k' \end{pmatrix} = 0 \;.$$

A solution of this equation for an independent normal vibration of the lattice is a plane wave

$$(1.10)\qquad \underline{v}\begin{pmatrix} l \\ k \end{pmatrix} = \underline{V}(k)\, e^{-i\omega t}\, e^{i(\underline{q}\cdot\underline{r}^{l})} \;.$$

Then from (1.9)

$$\omega^2 V_\alpha(k) - \sum_{k'}\sum_{\beta} D_{\alpha\beta}\binom{q}{kk'} V_\beta(k') = 0 \tag{1.11}$$

and
$$D_{\alpha\beta}\binom{q}{kk'} = \sum_{l'} D_{\alpha\beta}\binom{l-l'}{kk'} e^{-i(q.(r^l - r^{l'}))}$$

$$= \sum_{l} D_{\alpha\beta}\binom{l}{kk'} e^{-i(q.r^l)} \;; \tag{1.12}$$

D(q) is the representation of the dynamical matrix in reciprocal space.

The equations of motion (1.11) for a wave-vector $\underline{q}$ in the reciprocal space of the lattice are a set of 3s homogeneous equations in the reduced amplitudes $\underline{V}_\alpha(k)$. The necessary and sufficient condition that this set should have a non-trivial solution is that

$$\left| D(q) - \omega^2 I \right| = 0 \tag{1.13}$$

where I is the unit matrix of order $3s \times 3s$. For a particular wave-vector q, the characteristic equation (1.13) has 3s roots $\omega_j$. Three of these roots, the acoustic branches, as functions of q, tend to zero as $\underline{q} \to 0$. The remaining $3s - 3$ roots, the optical branches, tend to finite limits as $\underline{q} \to 0$. These 3s-3 limiting frequencies are the first-order Raman spectrum of the lattice. The intensities of the lines of this spectrum depend on the symmetry of the lattice. Born & Bradburn (1947) have shown that if each lattice point is a centre of symmetry then the intensities vanish and the first-order Raman spectrum does not exist.

The elements of the matrix $\mathcal{D}\binom{l-l'}{kk'}$ are related through the symmetry of the lattice in the following way.

A lattice point is defined by the vector $\underline{r}\binom{l}{k}$ referred to rectangular axes. A symmetry operation of the lattice can be expressed as a transformation matrix T, and if $\binom{L}{K}$ is some other lattice point,

(1.14) $$\underline{r}\binom{L}{K} = T\,\underline{r}\binom{l}{k} .$$

The elements of the matrix $\mathcal{D}\binom{l-l'}{kk'}$ will then have the transformation law

(1.15) $$\mathcal{D}\binom{L-L'}{KK'} = T\,\mathcal{D}\binom{l-l'}{kk'}\,\tilde{T}$$

where $\tilde{T}$ is the transpose of T and the change of indices $\binom{l}{k}$ is obtained from (1.14).

Further, since the potential energy $\Phi$ of the lattice is invariant for rigid translations and rotations,

(1.16) $$\sum_{l'k'} D_{\alpha\beta}\binom{l'}{kk'} = 0 ,$$

(1.17) $$\sum_{l,k} D_{\alpha\beta}\binom{l-l'}{kk'} x_{\lambda}\binom{l}{k} = \sum_{l,k} D_{\lambda\beta}\binom{l-l'}{kk'} x_{\alpha}\binom{l}{k} .$$

Ffom (1.16) we can define the matrix $\mathcal{D}\binom{0}{kk}$ representing the force of a point $\binom{l}{k}$ on itself as

(1.18) $$D_{\alpha\beta}\binom{0}{kk} = -\sum_{l'k'}{}' D_{\alpha\beta}\binom{l'}{kk'}$$

where the dash on the summation sign indicates that the terms in which $l' = 0$ , $k = k'$, are to be omitted.

The choice of possible wave-vectors $\underline{q}$ is restricted by the "cyclic lattice" condition, (Born (1923)).

The basic vectors $\underline{b}_\alpha$ of the reciprocal lattice are given by

$$(1.19)\quad \begin{cases} \underline{a}_\alpha \cdot \underline{b}_\beta = \begin{cases} 1 & \text{if } \alpha = \beta \\ 0 & \text{if } \alpha \neq \beta \end{cases} \\ \text{i.e. } \underline{b}_1 = \dfrac{\underline{a}_2 \wedge \underline{a}_3}{\underline{a}_1 \cdot \underline{a}_2 \wedge \underline{a}_3} \; ; \; \underline{b}_2 = \dfrac{\underline{a}_3 \wedge \underline{a}_1}{\underline{a}_1 \cdot \underline{a}_2 \wedge \underline{a}_3} \; ; \; \underline{b}_3 = \dfrac{\underline{a}_1 \wedge \underline{a}_2}{\underline{a}_1 \cdot \underline{a}_2 \wedge \underline{a}_3} \end{cases}$$

So if $\underline{r}^l = l^1 \underline{a}_1 + l^2 \underline{a}_2 + l^3 \underline{a}_3$

and

$$(1.20)\quad \begin{cases} \underline{q} = q_1 \underline{b}_1 + q_2 \underline{b}_2 + q_3 \underline{b}_3 \\ (q_1, q_2, q_3 \text{ integers}) \end{cases}$$

is a vector to a reciprocal lattice point, then the scalar product

$$(1.21)\quad \underline{q} \cdot \underline{r}^l = q_1 l^1 + q_2 l^2 + q_3 l^3$$

is an integer. Hence $e^{i(\underline{q} \cdot \underline{r}^l)}$ is periodic in reciprocal space.

The condition of the cyclic lattice expressing this periodicity can be written

$$(1.22)\quad \begin{cases} \underline{q} = 2\pi q_1 \underline{b}_1 + 2\pi q_2 \cdot \underline{b}_2 + 2\pi q_3 \cdot \underline{b}_3 \\ q_1 = \dfrac{h_1}{n}, \quad q_2 = \dfrac{h_2}{n}, \quad q_3 = \dfrac{h_3}{n} \end{cases}$$

where $h_1, h_2, h_3 = 0, 1, 2, \ldots\ldots, (n-1)$.

(b) Derivation of the elastic constants.

A solution of the equation of motion (1.9) for long-wave acoustical vibrations is

(1.23) $\underline{v}\binom{l}{k} = \underline{W}(k)\, e^{-i\omega t} e^{i(q \cdot \underline{r}\binom{l}{k})}$ .

(1.24) So $\underline{V}(k) = \underline{W}(k) . e^{i(q \cdot \underline{r}_k)}$

and (1.9) becomes

(1.25) $\omega^2 W_\alpha(k) - \sum_{k'} \sum_\beta C_{\alpha\beta}\binom{q}{kk'} W_\beta(k') = 0$

with $C_{\alpha\beta}\binom{q}{kk'} = D_{\alpha\beta}\binom{q}{kk'} e^{-i(q \cdot (\underline{r}_k - \underline{r}_{k'}))}$

(1.26) $= \sum_l D_{\alpha\beta}\binom{l}{kk'} . e^{-i(q \cdot \underline{r}\binom{l}{kk'})}$ .

Let $\omega^2 = \Omega$ , then (1.25) can be written

(1.27) $\Omega \underline{W} = C(q) . \underline{W}$ .

$\Omega$ , $\underline{W}$ and C(q) can be expanded in powers of the wave-vector $\underline{q}$ : for C(q) we have, in rectangular components of $\underline{q}$,

(1.28) $$\begin{cases} \overset{(0)}{C}_{\alpha\beta}\binom{q}{kk'} = \sum_l D_{\alpha\beta}\binom{l}{kk'} , \\ \overset{(1)}{C}_{\alpha\beta}\binom{q}{kk'} = -i \sum_l \sum_\gamma D_{\alpha\beta}\binom{l}{kk'} x_\gamma\binom{l}{kk'} q_\gamma , \\ \overset{(2)}{C}_{\alpha\beta}\binom{q}{kk'} = -\frac{1}{2} \sum_l \sum_{\lambda\mu} D_{\alpha\beta}\binom{l}{kk'} x_\lambda\binom{l}{kk'} x_\mu\binom{l}{kk'} q_\lambda q_\mu . \end{cases}$$

Equating terms containing like powers of $\underline{q}$ on either side of (1.27), we obtain, following Born & Begbie (1947), two approximations to the equations of motion (1.27). Written in matrix elements these are

(1.29) $\sum_\beta \sum_{k'} \overset{(0)}{C}_{\alpha\beta}\binom{q}{kk'} \overset{(1)}{W}_\beta(k') + \sum_\beta \sum_{k'} \sqrt{m_{k'}}\, \overset{(1)}{C}_{\alpha\beta}\binom{q}{kk'} W_\beta = 0$ ;

$$(1.30)\quad \Big(\sum_k m_k\Big)\overset{(2)}{\Omega}W_\alpha = \sum_{kk'}\sum_\beta \sqrt{m_k}\,\overset{(1)}{C}_{\alpha\beta}\binom{q}{kk'}\overset{(1)}{W}_\beta(k') + \sum_{kk'}\sqrt{m_k m_{k'}}\cdot\overset{(2)}{C}_{\alpha\beta}\binom{q}{kk'}W_\beta .$$

$W_\alpha$ ($\alpha = 1,2,3$) are three arbitrary constants, trivial solutions of (1.27) corresponding to the three possible independent translations of the crystal as a whole.

Put $\overset{(2)}{\Omega} = \omega^2$ and eliminate $\overset{(1)}{W}_\beta(k')$ between (1.29) and (1.30); the result may be written

$$(1.31)\qquad \rho\,\omega^2 W_\alpha = \sum_\beta D'_{\alpha\beta}(q)\,W_\beta$$

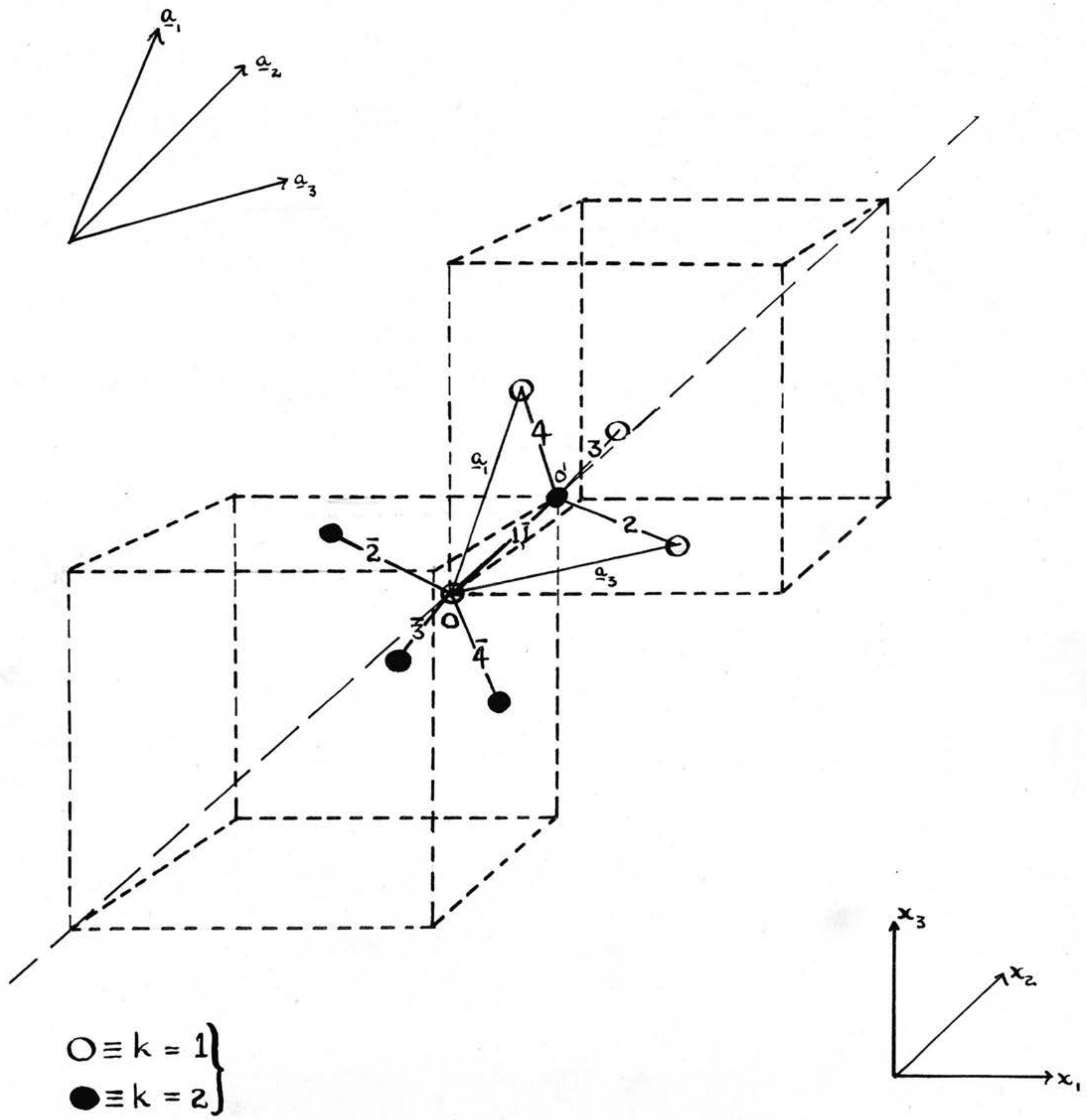
where $\rho = \frac{1}{v_a}\sum_k m_k$ is the density and $v_a = \underline{a}_1\cdot\underline{a}_2\wedge\underline{a}_3$ is the volume of the unit cell.

Comparison of (1.31) with the equation for the amplitudes of elastic waves in elasticity theory shows that the $D'_{\alpha\beta}(q)$ are related to the elastic constants in the following way:

$$\begin{bmatrix} D'_{11}(q)\\ D'_{22}(q)\\ D'_{33}(q)\\ D'_{23}(q)\\ D'_{31}(q)\\ D'_{12}(q)\end{bmatrix} = \begin{bmatrix} c_{11} & c_{66} & c_{55} & c_{65} & c_{51} & c_{16}\\ c_{66} & c_{22} & c_{44} & c_{24} & c_{46} & c_{62}\\ c_{55} & c_{44} & c_{33} & c_{43} & c_{35} & c_{54}\\ c_{65} & c_{24} & c_{43} & \frac{1}{2}(c_{23}+c_{44}) & \frac{1}{2}(c_{45}+c_{36}) & \frac{1}{2}(c_{64}+c_{25})\\ c_{51} & c_{46} & c_{35} & \frac{1}{2}(c_{45}+c_{36}) & \frac{1}{2}(c_{31}+c_{55}) & \frac{1}{2}(c_{56}+c_{14})\\ c_{16} & c_{62} & c_{54} & \frac{1}{2}(c_{64}+c_{25}) & \frac{1}{2}(c_{56}+c_{14}) & \frac{1}{2}(c_{12}+c_{66})\end{bmatrix}\cdot\begin{bmatrix} q_1^2\\ q_2^2\\ q_3^2\\ 2q_2q_3\\ 2q_3q_1\\ 2q_1q_2\end{bmatrix} \quad\ldots\ldots.(1.32)$$

Hence the elastic constants may be expressed in terms of the elements of the dynamical matrix of the lattice.

## FIGURE 1




FIRST NEIGHBOURS OF THE TWO CARBON ATOMS

IN THE UNIT CELL OF DIAMOND.

## 2. ELASTIC CONSTANTS OF DIAMOND.

The diamond crystal is built up of carbon atoms lying on two equal inter-penetrating face-centred cubic lattices, relatively displaced one-quarter of the way along a cube diagonal. The unit cell contains two atoms, one on each lattice: the distance between them is $a\sqrt{3}/2$, where 2a is the lattice constant of diamond ($= 3.56\times10^{-8}$ cm.).

Referred to a rectangular coordinate system with origin at a lattice point and axes parallel to the edges of the cubes, the cell-vectors of the lattice are

$$\left\{\begin{aligned} \underline{a}_1 &= a(\,0\,,1\,,1\,) \\ \underline{a}_2 &= a(\,1\,,0\,,1\,) \\ \underline{a}_3 &= a(\,1\,,1\,,0\,)\,. \end{aligned}\right. \tag{2.1}$$

The coordinates of the two atoms in the unit cell are $(0,0,0)$ and $(a/2,a/2,a/2)$: these atoms are labelled 0 and 0' in figure 1. Atoms lying on the same cubic lattice as 0 are labelled $k=1$, and those lying on the same cubic lattice as 0' are labelled $k=2$. Each atom has four nearest neighbours arranged tetrahedrally at a distance $a\sqrt{3}/2$. We assume as a first approximation that the elements of the dynamical matrix are negligibly small except for first neighbours: then the symbol $\ell$ may be used to number these neighbours, in place of the symbol $\binom{\ell}{kk'}$.

Table 1 gives the coordinates of the nearest neighbours of 0 and 0', the corresponding number $\ell$ and the integers $\ell^1, \ell^2, \ell^3$ given by

$$(1.1) \qquad \underline{r}^{\ell} = \ell^1 \underline{a}_1 + \ell^2 \underline{a}_2 + \ell^3 \underline{a}_3 .$$

Table 1.

| | $x_1$ | $x_2$ | $x_3$ | $k$ | $\ell$ | $\ell^1$ | $\ell^2$ | $\ell^3$ | $kk'$ |
|---|---|---|---|---|---|---|---|---|---|
| FIRST | $a/2$ | $a/2$ | $a/2$ | 2 | $\bar{1}$ | 0 | 0 | 0 | 21 |
| NEIGHBOURS | $-a/2$ | $-a/2$ | $a/2$ | 2 | $\bar{2}$ | 0 | 0 | $-1$ | 21 |
| OF O. | $-a/2$ | $a/2$ | $-a/2$ | 2 | $\bar{3}$ | 0 | $-1$ | 0 | 21 |
| | $a/2$ | $-a/2$ | $-a/2$ | 2 | $\bar{4}$ | $-1$ | 0 | 0 | 21 |
| FIRST | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 12 |
| NEIGHBOURS | a | a | 0 | 1 | 2 | 0 | 0 | 1 | 12 |
| OF O'. | a | 0 | a | 1 | 3 | 0 | 1 | 0 | 12 |
| | 0 | a | a | 1 | 4 | 1 | 0 | 0 | 12 |

The symmetry operations of the diamond lattice can be described by six transformation matrices.

$\underline{A}_1$: The lattice has a threefold axis of rotation $x_1 = x_2 = x_3$, so

$$(2.2) \qquad T_1 = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix} .$$

The change of label $\ell$, in the notation of substitution groups is

$$(2.3) \qquad \begin{cases} (1) & (32) & (43) & (24) \\ (\bar{1}) & (\bar{3}\bar{2}) & (\bar{4}\bar{3}) & (\bar{2}\bar{4}) \end{cases} .$$

$\underline{A}_2$ : There is a centre of inversion at the point $x_1 = x_2 = x_3 = a/4$ : this is equivalent to a centre of inversion at (0,0,0) and a translation $x_1 = x_2 = x_3 = a/2$.

Hence

(2.4)
$$\left\{\begin{array}{l} T_2 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \\ \text{and} \quad (\bar{1}\,1) \quad (\bar{2}\,2) \quad (\bar{3}\,3) \quad (\bar{4}\,4) \end{array}\right.$$

$\underline{A}_3$ : There are three planes of reflection. One is $x_1 = x_2$ giving

(2.5)
$$\left\{\begin{array}{l} T_3 = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \\ \text{and} \quad \begin{array}{lll} (1) & (2) & (4\,3) \\ (\bar{1}) & (\bar{2}) & (\bar{4}\,\bar{3}) \end{array} \end{array}\right.$$

The other two planes of reflection $x_2 = x_3$ and $x_3 = x_1$ can be obtained from $\underline{A}_1$ and $\underline{A}_3$ .

$\underline{A}_4$ : A rotation through $\pi/2$ about an axis through the point (a/2,a/2,a/2) parallel to the $x_3$-axis followed by a rotation through $\pi/2$ about an axis through the same point parallel to the $x_1$-axis, gives

(2.6)
$$\left\{\begin{array}{l} T_4 = \begin{bmatrix} 0 & -1 & 0 \\ 0 & 0 & -1 \\ 1 & 0 & 0 \end{bmatrix} \\ \text{and} \quad \begin{array}{llll} (3) & (2\,1) & (4\,2) & (1\,4) \\ (\bar{3}) & (\bar{2}\,\bar{1}) & (\bar{4}\,\bar{2}) & (\bar{1}\,\bar{4}) \end{array} \end{array}\right.$$

$\underline{A}_5$: A rotation through $\pi/2$ about an axis parallel to the $x_1$-axis through the point (a/2,a/2,a/2) followed by a rotation through $\pi/2$ about an axis through the same point parallel to the $x_2$-axis, gives

$$(2.7)\quad \left\{ \begin{array}{l} T_5 = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & -1 \\ -1 & 0 & 0 \end{bmatrix} \\ \text{and} \quad \begin{matrix} (2) & (41) & (13) & (34) \\ (\bar{2}) & (\bar{4}\bar{1}) & (\bar{1}\bar{3}) & (\bar{3}\bar{4}) \end{matrix} \end{array} \right. .$$

$\underline{A}_6$ : A rotation through $\pi/2$ about an axis parallel to the $x_2$-axis through the point $(a/2, a/2, a/2)$, followed by a rotation through $\pi/2$ about an axis through the same point parallel to the $x_3$-axis, gives

$$(2.8)\quad \left\{ \begin{array}{l} T_6 = \begin{bmatrix} 0 & -1 & 0 \\ 0 & 0 & 1 \\ -1 & 0 & 0 \end{bmatrix} \\ \text{and} \quad \begin{matrix} (4) & (31) & (12) & (23) \\ (\bar{4}) & (\bar{3}\bar{1}) & (\bar{1}\bar{2}) & (\bar{2}\bar{3}) \end{matrix} \end{array} \right. .$$

To these are added the symmetry conditions of the dynamical matrix: from (1.5)

$$(2.9)\quad D_{\alpha\beta}\binom{l}{kk'} = D_{\beta\alpha}\binom{-l}{k'k}.$$

From $\underline{A}_2$, $D^{\bar{l}} = T_2 D^l \tilde{T}_2 = D^l$, i.e.

$$(2.10)\quad \left\{ \begin{array}{lll} D^1 = D^{\bar{1}} & : & D^2 = D^{\bar{2}} \; : \\ D^3 = D^{\bar{3}} & : & D^4 = D^{\bar{4}} \; . \end{array} \right.$$

From (2.9) and Table 1,

$$(2.11)\quad \left\{ \begin{array}{l} D^1 = \tilde{D}^{\bar{1}} = \tilde{D}^1 \\ D^2 = \tilde{D}^{\bar{2}} = \tilde{D}^2 \\ D^3 = \tilde{D}^{\bar{3}} = \tilde{D}^3 \\ D^4 = \tilde{D}^{\bar{4}} = \tilde{D}^4 \end{array} \right. .$$

Thus all the matrices $D^{\ell}$ are symmetric.

From $\underline{A}_1$, since $D^1$ is invariant with respect to $T_1$,

$$(2.12)\qquad \begin{cases} D^1_{11} = D^1_{22} = D^1_{33} \\ D^1_{12} = D^1_{13} = D^1_{23} . \end{cases}$$

So we may put

$$(2.13)\qquad \left.\begin{matrix} D^1 \\ D^{\bar{1}} \end{matrix}\right\} = -\frac{1}{m}\begin{bmatrix} \alpha & \beta & \beta \\ \beta & \alpha & \beta \\ \beta & \beta & \alpha \end{bmatrix}$$

where m = mass of carbon atom.

From $\underline{A}_4$,

$$(2.14)\qquad \left.\begin{matrix} D^2 \\ D^{\bar{2}} \end{matrix}\right\} = T_4 D^1 \tilde{T}_4 = -\frac{1}{m}\begin{bmatrix} \alpha & \beta & -\beta \\ \beta & \alpha & -\beta \\ -\beta & -\beta & \alpha \end{bmatrix}.$$

By repeated application of $\underline{A}_1$ we find

$$(2.15)\qquad \left.\begin{matrix} D^3 \\ D^{\bar{3}} \end{matrix}\right\} = T_1 D^2 \tilde{T}_1 = -\frac{1}{m}\begin{bmatrix} \alpha & -\beta & \beta \\ -\beta & \alpha & -\beta \\ \beta & -\beta & \alpha \end{bmatrix},$$

$$(2.16)\qquad \left.\begin{matrix} D^4 \\ D^{\bar{4}} \end{matrix}\right\} = T_1 D^3 \tilde{T}_1 = -\frac{1}{m}\begin{bmatrix} \alpha & -\beta & -\beta \\ -\beta & \alpha & \beta \\ -\beta & \beta & \alpha \end{bmatrix}.$$

These eight matrices $D^{\ell}$ and $D^{\bar{\ell}}$ ( $\ell$=1,2,3,4) satisfy all the other relations which may be deduced from the symmetry operations.

Lastly, from (1.18)

$$\mathcal{D}\begin{pmatrix}0\\11\end{pmatrix} = \mathcal{D}\begin{pmatrix}0\\22\end{pmatrix} = \frac{4\alpha}{m}\begin{bmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix}. \tag{2.17}$$

We now proceed to calculate the matrices $C\begin{pmatrix}q\\kk'\end{pmatrix}$ from the relation

$$C_{\alpha\beta}\begin{pmatrix}q\\kk'\end{pmatrix} = \sum_{l} D_{\alpha\beta}\begin{pmatrix}l\\kk'\end{pmatrix} e^{-i\left(q\cdot r\begin{pmatrix}l\\kk'\end{pmatrix}\right)}. \tag{1.26}$$

Table 2 gives the values of the rectangular components of $\underline{r}\begin{pmatrix}l\\kk'\end{pmatrix}$ for the first neighbours of 0 and 0'.

<u>Table 2.</u>

| $r \backslash l$ | 1 | 2 | 3 | 4 | $r \backslash l$ | $\bar{1}$ | $\bar{2}$ | $\bar{3}$ | $\bar{4}$ |
|---|---|---|---|---|---|---|---|---|---|
| $x_1\begin{pmatrix}l\\12\end{pmatrix}$ | $-\frac{a}{2}$ | $\frac{a}{2}$ | $\frac{a}{2}$ | $-\frac{a}{2}$ | $x_1\begin{pmatrix}l\\21\end{pmatrix}$ | $\frac{a}{2}$ | $-\frac{a}{2}$ | $-\frac{a}{2}$ | $\frac{a}{2}$ |
| $x_2\begin{pmatrix}l\\12\end{pmatrix}$ | $-\frac{a}{2}$ | $\frac{a}{2}$ | $-\frac{a}{2}$ | $\frac{a}{2}$ | $x_2\begin{pmatrix}l\\21\end{pmatrix}$ | $\frac{a}{2}$ | $-\frac{a}{2}$ | $\frac{a}{2}$ | $-\frac{a}{2}$ |
| $x_3\begin{pmatrix}l\\12\end{pmatrix}$ | $-\frac{a}{2}$ | $-\frac{a}{2}$ | $\frac{a}{2}$ | $\frac{a}{2}$ | $x_3\begin{pmatrix}l\\21\end{pmatrix}$ | $\frac{a}{2}$ | $\frac{a}{2}$ | $-\frac{a}{2}$ | $-\frac{a}{2}$ |

Since $\mathcal{D}^{l} = \mathcal{D}^{\bar{l}}$ and $\underline{r}^{l} = -\underline{r}^{\bar{l}}$,

$$C\begin{pmatrix}q\\12\end{pmatrix} = C\begin{pmatrix}-q\\21\end{pmatrix}. \tag{2.18}$$

Expanding in powers of $q$, we find

$$\left\{\begin{aligned} \overset{(0)}{C}\begin{pmatrix}q\\12\end{pmatrix} &= \overset{(0)}{C}\begin{pmatrix}q\\21\end{pmatrix}\\ \overset{(1)}{C}\begin{pmatrix}q\\12\end{pmatrix} &= -\overset{(1)}{C}\begin{pmatrix}q\\21\end{pmatrix}\\ \overset{(2)}{C}\begin{pmatrix}q\\12\end{pmatrix} &= \overset{(2)}{C}\begin{pmatrix}q\\21\end{pmatrix} \end{aligned}\right. \tag{2.19}$$

,

so it is only necessary to calculate the expansion of $C\binom{q}{12}$.

Also,

$$(2.20)\quad \begin{cases} \overset{(0)}{C}\binom{q}{11} = \overset{(0)}{C}\binom{q}{22} = D\binom{0}{11} = D\binom{0}{22}, \\ \overset{(1)}{C}\binom{q}{11} = \overset{(1)}{C}\binom{q}{22} \doteq 0, \\ \overset{(2)}{C}\binom{q}{11} = \overset{(2)}{C}\binom{q}{22} = 0. \end{cases}$$

The expansion of $C\binom{q}{12}$ is

$$(2.21)\quad C\binom{q}{12} = \sum_{l=1,2,3,4} D^l . e^{-i(q.\underline{r}^l)} .$$

Hence

$$(2.22)\quad \overset{(0)}{C}\binom{q}{12} = -\frac{4\alpha}{m}\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix},$$

$$(2.23)\quad \overset{(1)}{C}\binom{q}{12} = -\frac{2ia}{m}.\beta \begin{bmatrix} 0 & q_z & q_y \\ q_z & 0 & q_x \\ q_y & q_x & 0 \end{bmatrix},$$

$$(2.24)\quad \overset{(2)}{C}\binom{q}{12} = \frac{a^2}{2m}\begin{bmatrix} \alpha(q_x^2+q_y^2+q_z^2) & 2\beta q_x q_y & 2\beta q_z q_x \\ 2\beta q_x q_y & \alpha(q_x^2+q_y^2+q_z^2) & 2\beta q_y q_z \\ 2\beta q_z q_x & 2\beta q_y q_z & \alpha(q_x^2+q_y^2+q_z^2) \end{bmatrix}$$

$$(2.25)\quad \overset{(0)}{C}\binom{q}{11} = \overset{(0)}{C}\binom{q}{22} = \frac{4\alpha}{m}\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

Substituting these matrices in the equation

(1.29),

$$\frac{4\alpha}{m}\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}\left(\overset{(1)}{W}(1) - \overset{(1)}{W}(2)\right) + \sqrt{m}\left(-\frac{2ia}{m}\beta\right)\begin{bmatrix} 0 & q_z & q_y \\ q_z & 0 & q_x \\ q_y & q_x & 0 \end{bmatrix}.\underline{W} = 0,$$

and
$$\overset{(1)}{W}(1) - \overset{(1)}{W}(2) = \frac{ia\sqrt{m}}{2} \cdot \frac{\beta}{\alpha} \begin{bmatrix} 0 & q_z & q_y \\ q_z & 0 & q_x \\ q_y & q_x & 0 \end{bmatrix} \cdot \underline{W} \cdot \tag{2.26}$$

Substituting (2.26) in (1.30),

$$2m\omega^2 \underline{W} = -a^2 \frac{\beta^2}{\alpha} \begin{bmatrix} 0 & q_z & q_y \\ q_z & 0 & q_x \\ q_y & q_x & 0 \end{bmatrix} \cdot \begin{bmatrix} 0 & q_z & q_y \\ q_z & 0 & q_x \\ q_y & q_x & 0 \end{bmatrix} \cdot \underline{W}$$

$$+ a^2 \begin{bmatrix} \alpha(q_x^2+q_y^2+q_z^2) & 2\beta q_x q_y & 2\beta q_z q_x \\ 2\beta q_x q_y & \alpha(q_x^2+q_y^2+q_z^2) & 2\beta q_y q_z \\ 2\beta q_z q_x & 2\beta q_y q_z & \alpha(q_x^2+q_y^2+q_z^2) \end{bmatrix} \cdot \underline{W}$$

$$\therefore \omega^2 \underline{W} = \frac{a^2}{2m} \begin{bmatrix} \alpha q_x^2 + (\alpha - \frac{\beta^2}{\alpha})(q_y^2+q_z^2) & \beta(2-\frac{\beta}{\alpha}) q_x q_y & \beta(2-\frac{\beta}{\alpha}) q_z q_x \\ \beta(2-\frac{\beta}{\alpha}) q_x q_y & \alpha q_y^2 + (\alpha - \frac{\beta^2}{\alpha})(q_z^2+q_x^2) & \beta(2-\frac{\beta}{\alpha}) q_y q_z \\ \beta(2-\frac{\beta}{\alpha}) q_z q_x & \beta(2-\frac{\beta}{\alpha}) q_y q_z & \alpha q_z^2 + (\alpha - \frac{\beta^2}{\alpha})(q_x^2+q_y^2) \end{bmatrix} \cdot \underline{W}$$

.....(2.27)

This has the form $\omega^2 \underline{W} = \frac{1}{\rho} D'(q) \cdot \underline{W}$ where

$$\begin{bmatrix} D'_{11}(q) \\ D'_{22}(q) \\ D'_{33}(q) \\ D'_{23}(q) \\ D'_{31}(q) \\ D'_{12}(q) \end{bmatrix} = \rho \frac{a^2}{2m} \begin{bmatrix} \alpha & \alpha - \frac{\beta^2}{\alpha} & \alpha - \frac{\beta^2}{\alpha} & 0 & 0 & 0 \\ \alpha - \frac{\beta^2}{\alpha} & \alpha & \alpha - \frac{\beta^2}{\alpha} & 0 & 0 & 0 \\ \alpha - \frac{\beta^2}{\alpha} & \alpha - \frac{\beta^2}{\alpha} & \alpha & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2}\beta(2-\frac{\beta}{\alpha}) & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{2}\beta(2-\frac{\beta}{\alpha}) & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2}\beta(2-\frac{\beta}{\alpha}) \end{bmatrix} \cdot \begin{bmatrix} q_x^2 \\ q_y^2 \\ q_z^2 \\ 2q_y q_z \\ 2q_z q_x \\ 2q_x q_y \end{bmatrix}$$

.....(2.28)

The unit cell has volume $v_a = \underline{a}_1 \cdot \underline{a}_2 \wedge \underline{a}_3 = 2a^3$. So the density $\rho = \frac{2m}{2a^3} = \frac{m}{a^3}$.

Comparing (2.28) with (1.32) we find the elastic constants are

$$(2.29) \quad \begin{cases} c_{11} = c_{22} = c_{33} = \frac{1}{2a}\alpha , \\ c_{44} = c_{55} = c_{66} = \frac{1}{2a}\left(\alpha - \frac{\beta^2}{\alpha}\right), \\ c_{12} = c_{13} = c_{23} = \frac{1}{2a}(2\beta - \alpha) . \end{cases}$$

The remaining elastic constants vanish.

Solving (2.29) for $\alpha$ and $\beta$,

$$(2.30) \quad \begin{cases} \alpha = 2ac_{11} , \\ \beta = a(c_{11} + c_{12}) . \end{cases}$$

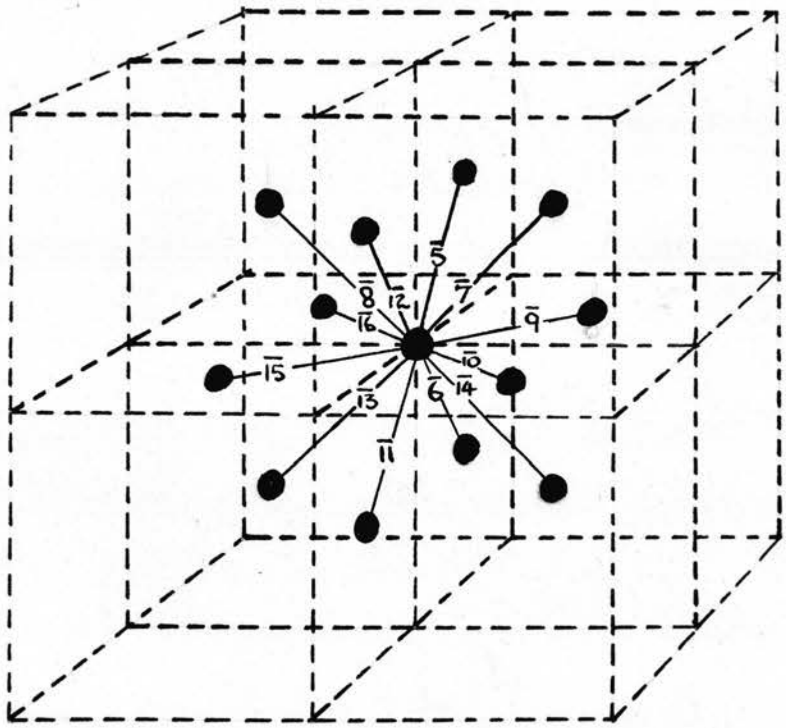
The elastic constants satisfy the quadratic relation

$$(2.31) \qquad 4c_{11}(c_{11} - c_{44}) = (c_{11} + c_{12})^2 .$$

This quadratic relation has been obtained already by Born (1914), using as repeating unit a cube of side 2a containing 8 carbon atoms and considering as here only forces between any carbon atom and its four nearest neighbours.

Now the atoms O and O' in the unit cell (fig. 1) have each 12 second neighbours at a distance $a\sqrt{2}$, lying on the same face-centred cubic lattice. As a second approximation let us consider in addition to the first neighbour elements, the elements of the dynamical matrix corresponding to these second neighbours.

FIGURE 2




SECOND NEIGHBOURS OF THE ATOM "O"

IN THE UNIT CELL.

Figure 2 shows the second neighbours of the atom 0; Table 3 specifies the coordinates and labelling of these neighbours and Table 4 the integers $l^1, l^2, l^3$ given by $\underline{r}^l = l^1\underline{a}_1 + l^2\underline{a}_2 + l^3\underline{a}_3$.

**Table 3.**

| | $x_1$ | $x_2$ | $x_3$ | $k$ | $l$ | | $x_1$ | $x_2$ | $x_3$ | $k$ | $l$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| SECOND NEIGHBOURS OF 0 | $0$ | $a$ | $a$ | 1 | $\bar{5}$ | SECOND NEIGHBOURS OF 0' | $a/2$ | $-a/2$ | $-a/2$ | 2 | 5 |
| | $0$ | $a$ | $-a$ | 1 | $\bar{6}$ | | $a/2$ | $-a/2$ | $3a/2$ | 2 | 6 |
| | $a$ | $0$ | $a$ | 1 | $\bar{7}$ | | $-a/2$ | $a/2$ | $-a/2$ | 2 | 7 |
| | $-a$ | $0$ | $a$ | 1 | $\bar{8}$ | | $3a/2$ | $a/2$ | $-a/2$ | 2 | 8 |
| | $a$ | $a$ | $0$ | 1 | $\bar{9}$ | | $-a/2$ | $-a/2$ | $a/2$ | 2 | 9 |
| | $a$ | $-a$ | $0$ | 1 | $\overline{10}$ | | $-a/2$ | $3a/2$ | $a/2$ | 2 | 10 |
| | $0$ | $-a$ | $-a$ | 1 | $\overline{11}$ | | $a/2$ | $3a/2$ | $3a/2$ | 2 | 11 |
| | $0$ | $-a$ | $a$ | 1 | $\overline{12}$ | | $a/2$ | $3a/2$ | $-a/2$ | 2 | 12 |
| | $-a$ | $0$ | $-a$ | 1 | $\overline{13}$ | | $3a/2$ | $a/2$ | $3a/2$ | 2 | 13 |
| | $a$ | $0$ | $-a$ | 1 | $\overline{14}$ | | $-a/2$ | $a/2$ | $3a/2$ | 2 | 14 |
| | $-a$ | $-a$ | $0$ | 1 | $\overline{15}$ | | $3a/2$ | $3a/2$ | $a/2$ | 2 | 15 |
| | $-a$ | $a$ | $0$ | 1 | $\overline{16}$ | | $3a/2$ | $-a/2$ | $a/2$ | 2 | 16 |

**Table 4.**

| $l$ | $\bar{5}$ | $\bar{6}$ | $\bar{7}$ | $\bar{8}$ | $\bar{9}$ | $\overline{10}$ | $\overline{11}$ | $\overline{12}$ | $\overline{13}$ | $\overline{14}$ | $\overline{15}$ | $\overline{16}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 11 | 12 | 13 | 14 | 15 | 16 | 5 | 6 | 7 | 8 | 9 | 10 |
| $l^1$ | 1 | 0 | 0 | 1 | 0 | −1 | −1 | 0 | 0 | −1 | 0 | 1 |
| $l^2$ | 0 | −1 | 1 | 0 | 0 | 1 | 0 | 1 | −1 | 0 | 0 | −1 |
| $l^3$ | 0 | 1 | 0 | −1 | 1 | 0 | 0 | −1 | 0 | 1 | −1 | 0 |
| $kk'$ | 11 | 11 | 11 | 11 | 11 | 11 | 11 | 11 | 11 | 11 | 11 | 11 |
| | 22 | 22 | 22 | 22 | 22 | 22 | 22 | 22 | 22 | 22 | 22 | 22 |

The 24 matrices $D^{l}$ and $D^{\bar{l}}$ ($l = 5,6,7\dots,16$) can be expressed in terms of three constants $\lambda$, $\mu$, $\nu$ by using the transformation matrices T ((2.2)....(2.8)) as for the first-neighbour matrices $D^{l}$.

Then

$$\left.\begin{matrix} D^{5} = D^{\bar{5}} \\ D^{11} = D^{\bar{11}} \end{matrix}\right\} = -\frac{1}{m}\begin{bmatrix} \lambda & 0 & 0 \\ 0 & \mu & \nu \\ 0 & \nu & \mu \end{bmatrix} \qquad \left.\begin{matrix} D^{6} = D^{\bar{6}} \\ D^{12} = D^{\bar{12}} \end{matrix}\right\} = -\frac{1}{m}\begin{bmatrix} \lambda & 0 & 0 \\ 0 & \mu & -\nu \\ 0 & -\nu & \mu \end{bmatrix}$$

$$\left.\begin{matrix} D^{7} = D^{\bar{7}} \\ D^{13} = D^{\bar{13}} \end{matrix}\right\} = -\frac{1}{m}\begin{bmatrix} \mu & 0 & \nu \\ 0 & \lambda & 0 \\ \nu & 0 & \mu \end{bmatrix} \qquad \left.\begin{matrix} D^{8} = D^{\bar{8}} \\ D^{14} = D^{\bar{14}} \end{matrix}\right\} = -\frac{1}{m}\begin{bmatrix} \mu & 0 & -\nu \\ 0 & \lambda & 0 \\ -\nu & 0 & \mu \end{bmatrix}$$

$$\left.\begin{matrix} D^{9} = D^{\bar{9}} \\ D^{15} = D^{\bar{15}} \end{matrix}\right\} = -\frac{1}{m}\begin{bmatrix} \mu & \nu & 0 \\ \nu & \mu & 0 \\ 0 & 0 & \lambda \end{bmatrix} \qquad \left.\begin{matrix} D^{10} = D^{\bar{10}} \\ D^{16} = D^{\bar{16}} \end{matrix}\right\} = -\frac{1}{m}\begin{bmatrix} \mu & -\nu & 0 \\ -\nu & \mu & 0 \\ 0 & 0 & \lambda \end{bmatrix}$$

.....(2.32)

From (1.18), (2.17) is replaced by

(2.33) $$D\binom{0}{11} = D\binom{0}{22} = \frac{4}{m}(\alpha+\lambda+2\mu)\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

Since $D^{l} = D^{\bar{l}}$ and $\underline{r}^{l} = -\underline{r}^{\bar{l}}$, the equations (2.18) and (2.19) still hold and the expansion of $C\binom{q}{12}$ is given as before by (2.22),(2.23) and (2.24).

But since $C\binom{q}{11} = C\binom{-q}{22}$, (2.20) is replaced by

(2.34) $$\begin{cases} \overset{(0)}{C}\binom{q}{11} = \overset{(0)}{C}\binom{q}{22}, \\ \overset{(1)}{C}\binom{q}{11} = -\overset{(1)}{C}\binom{q}{22}, \\ \overset{(2)}{C}\binom{q}{11} = \overset{(2)}{C}\binom{q}{22}. \end{cases}$$

Table 5 gives the rectangular components of $\underline{r}\binom{l}{kk'}$ for the second neighbours of O', since, from (2.34) it is necessary to calculate the expansion of $C\binom{q}{22}$ only.

Table 5.

| $r \backslash l$ | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $x_1\binom{l}{kk'}$ | 0 | 0 | $-a$ | $a$ | $-a$ | $-a$ | 0 | 0 | $a$ | $-a$ | $a$ | $a$ |
| $x_2\binom{l}{kk'}$ | $-a$ | $-a$ | 0 | 0 | $-a$ | $a$ | $a$ | $a$ | 0 | 0 | $a$ | $-a$ |
| $x_3\binom{l}{kk'}$ | $-a$ | $a$ | $-a$ | $-a$ | 0 | 0 | $a$ | $-a$ | $a$ | $a$ | 0 | 0 |
| $kk'$ | 22 | 22 | 22 | 22 | 22 | 22 | 22 | 22 | 22 | 22 | 22 | 22 |

Thus

(2.25) $$\overset{(0)}{C}\binom{q}{22} = \frac{4\alpha}{m}\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix},$$

(2.35) $$\overset{(1)}{C}\binom{q}{22} = 0 ,$$

(2.36) $$\overset{(2)}{C}\binom{q}{22} = \frac{2a^2}{m}\begin{bmatrix} 2\mu q_x^2 + (\lambda+\mu)(q_y^2+q_z^2) & 2\nu q_x q_y & 2\nu q_z q_x \\ 2\nu q_x q_y & 2\mu q_y^2 + (\lambda+\mu)(q_z^2+q_x^2) & 2\nu q_y q_z \\ 2\nu q_z q_x & 2\nu q_y q_z & 2\mu q_z^2 + (\lambda+\mu)(q_x^2+q_y^2) \end{bmatrix}.$$

Substituting again in (1.29), (2.26) remains unaltered, but (1.30) now leads to

$$\omega^2 \underline{W} = \frac{a^2}{2m}\begin{bmatrix} [\alpha+8\mu]q_x^2 + \left[\alpha-\frac{\beta^2}{\alpha}+4\overline{\lambda+\mu}\right][q_y^2+q_z^2] & \left[\beta(2-\frac{\beta}{\alpha})+8\nu\right]q_x q_y & \left[\beta(2-\frac{\beta}{\alpha})+8\nu\right]q_z q_x \\ \left[\beta(2-\frac{\beta}{\alpha})+8\nu\right]q_x q_y & [\alpha+8\mu]q_y^2 + \left[\alpha-\frac{\beta^2}{\alpha}+4\overline{\lambda+\mu}\right][q_z^2+q_x^2] & \left[\beta(2-\frac{\beta}{\alpha})+8\nu\right]q_y q_z \\ \left[\beta(2-\frac{\beta}{\alpha})+8\nu\right]q_z q_x & \left[\beta(2-\frac{\beta}{\alpha})+8\nu\right]q_y q_z & [\alpha+8\mu]q_z^2 + \left[\alpha-\frac{\beta^2}{\alpha}+4\overline{\lambda+\mu}\right][q_x^2+q_y^2] \end{bmatrix} \cdot \underline{W}$$

......(2.37)

i.e. $\quad \omega^2 \underline{W} = \frac{1}{\rho} D'(q) \cdot \underline{W}$ $\qquad$ and

$$\begin{bmatrix} D_{11}'(q) \\ D_{22}'(q) \\ D_{33}'(q) \\ D_{23}'(q) \\ D_{31}'(q) \\ D_{12}'(q) \end{bmatrix} = \rho \cdot \frac{a^2}{2m}\begin{bmatrix} \alpha+8\mu & \alpha-\beta^2/\alpha+4(\lambda+\mu) & \alpha-\beta^2/\alpha+4(\lambda+\mu) & 0 & 0 & 0 \\ \alpha-\beta^2/\alpha+4(\lambda+\mu) & \alpha+8\mu & \alpha-\beta^2/\alpha+4(\lambda+\mu) & 0 & 0 & 0 \\ \alpha-\beta^2/\alpha+4(\lambda+\mu) & \alpha-\beta^2/\alpha+4(\lambda+\mu) & \alpha+8\mu & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2}\beta(2-\beta/\alpha)+4\nu & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{2}\beta(2-\beta/\alpha)+4\nu & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2}\beta(2-\beta/\alpha)+4\nu \end{bmatrix} \cdot \begin{bmatrix} q_x^2 \\ q_y^2 \\ q_z^2 \\ 2q_y q_z \\ 2q_z q_x \\ 2q_x q_y \end{bmatrix}$$

.....(2.38)

Comparison with (1.32) gives

$$(2.39)\quad \begin{cases} C_{11} = C_{22} = C_{33} = \frac{1}{2a}(\alpha+8\mu), \\ C_{44} = C_{55} = C_{66} = \frac{1}{2a}\left(\alpha-\frac{\beta^2}{\alpha}+4\lambda+4\mu\right), \\ C_{12} = C_{13} = C_{23} = \frac{1}{2a}(2\beta-\alpha-4\lambda-4\mu+8\nu). \end{cases}$$

These equations (2.39), as they stand, cannot be solved to give the atomic constants in terms of the elastic constants and there is no relation between the elastic constants analogous to (2.31).

But if it is assumed that the forces between an atom and its second neighbours are central forces, then it is already known (Born (1940)) that for a simple face-centred cubic lattice under central forces, the elastic constants can be expressed in terms of one atomic constant, and

(2.40) $$c_{11} = 2c_{12} = 2c_{44}.$$

So taking the terms in (2.39) referring to second neighbour forces,

(2.41) $$\begin{cases} 8\mu = 2(4\alpha + 4\mu) = 2(-4\lambda - 4\mu + 8\nu), \\ \therefore\ \lambda = 0, \\ \mu = \nu. \end{cases}$$

The elastic constants in terms of $\alpha, \beta, \mu$ are then

(2.42) $$\begin{cases} c_{11} = c_{22} = c_{33} = \frac{1}{2a}(\alpha + 8\mu), \\ c_{44} = c_{55} = c_{66} = \frac{1}{2a}\left(\alpha - \frac{\beta^2}{\alpha} + 4\mu\right), \\ c_{12} = c_{13} = c_{23} = \frac{1}{2a}(2\beta - \alpha + 4\mu). \end{cases}$$

From (2.42) can be derived three quadratic expressions for $\alpha$, $\beta$, $\mu$ in terms of $c_{11}$, $c_{12}$, $c_{44}$, but there is no relation between the elastic constants.

## 3. FREQUENCY SPECTRUM OF DIAMOND.

The frequencies of vibration of diamond are obtained by solving the characteristic equation

(1.13) $$|D(q) - \omega^2 I| = 0$$

for various wave-vectors $\underline{q}$ in reciprocal space.

The cell-vectors of diamond are

(2.1) $$\begin{cases} \underline{a}_1 = a(\,0\,,\ 1\,,\ 1\,) \\ \underline{a}_2 = a(\,1\,,\ 0\,,\ 1\,) \\ \underline{a}_3 = a(\,1\,,\ 1\,,\ 0\,)\ . \end{cases}$$

Thus from (1.19) the cell-vectors of the reciprocal lattice are

(3.1) $$\begin{cases} \underline{b}_1 = \frac{1}{2a}(-1,\ +1,\ +1\ ) \\ \underline{b}_2 = \frac{1}{2a}(+1,\ -1,\ +1\ ) \\ \underline{b}_3 = \frac{1}{2a}(+1,\ +1,\ -1\ )\ . \end{cases}$$

The reciprocal lattice is a body-centred lattice.

The wave-vector $\underline{q}$ is then

(3.2) $$\underline{q} = \frac{1}{2a}\cdot 2\pi\left[(-q_1+q_2+q_3),\ (q_1-q_2+q_3),\ (q_1+q_2-q_3)\right]$$

or

(3.3) $$\underline{q} = \frac{1}{2a}\cdot 2\pi\left[q_x,\ q_y,\ q_z\right].$$

From the condition of the cyclic lattice (1.22) it is sufficient to take values of $\underline{q}$ in reciprocal space such that

(3.4) $$0 \le q_1, q_2, q_3 \le 1\ .$$

The elements of D(q) are obtained from (1.12) by substituting the matrices $\mathfrak{D}^{\ell}$ given by (2.13), (2.14), (2.15), (2.16), (2.32), (2.33), and the vectors $\underline{r}^{l}$ given by (1.1) and Tables 1 and 4.

They are as follows:

$$D_{11}\binom{q}{11} = D_{11}\binom{q}{22} = \frac{2}{m}\Big[2\alpha + \lambda\{2 - \cos 2\pi q_1 - \cos 2\pi(q_2 - q_3)\}$$
$$+ \mu\{4 - \cos 2\pi q_2 - \cos 2\pi q_3$$
$$- \cos 2\pi(q_1 - q_2) - \cos 2\pi(q_3 - q_1)\}\Big],$$

$$D_{22}\binom{q}{11} = D_{22}\binom{q}{22} = \frac{2}{m}\Big[2\alpha + \lambda\{2 - \cos 2\pi q_2 - \cos 2\pi(q_3 - q_1)\}$$
$$+ \mu\{4 - \cos 2\pi q_3 - \cos 2\pi q_1$$
$$- \cos 2\pi(q_2 - q_3) - \cos 2\pi(q_1 - q_2)\}\Big],$$

$$D_{33}\binom{q}{11} = D_{33}\binom{q}{22} = \frac{2}{m}\Big[2\alpha + \lambda\{2 - \cos 2\pi q_3 - \cos 2\pi(q_1 - q_2)\}$$
$$+ \mu\{4 - \cos 2\pi q_1 - \cos 2\pi q_2$$
$$- \cos 2\pi(q_3 - q_1) - \cos 2\pi(q_2 - q_3)\}\Big],$$

$$D_{12}\binom{q}{11} = D_{12}\binom{q}{22} = \frac{2\nu}{m}\Big[\cos 2\pi(q_1 - q_2) - \cos 2\pi q_3\Big],$$

$$D_{13}\binom{q}{11} = D_{13}\binom{q}{22} = \frac{2\nu}{m}\Big[\cos 2\pi(q_3 - q_1) - \cos 2\pi q_2\Big],$$

$$D_{23}\binom{q}{11} = D_{23}\binom{q}{22} = \frac{2\nu}{m}\Big[\cos 2\pi(q_2 - q_3) - \cos 2\pi q_1\Big],$$

$$D_{11}\binom{q}{12} = D_{22}\binom{q}{12} = D_{33}\binom{q}{12} = D^{*}_{11}\binom{q}{21} = D^{*}_{22}\binom{q}{21} = D^{*}_{33}\binom{q}{21}$$
$$= -\frac{\alpha}{m}\Big[1 + e^{-2\pi i q_3} + e^{-2\pi i q_2} + e^{-2\pi i q_1}\Big],$$

$$D_{12}\binom{q}{12} = D^{*}_{12}\binom{q}{21} = -\frac{\beta}{m}\Big[1 + e^{-2\pi i q_3} - e^{-2\pi i q_2} - e^{-2\pi i q_1}\Big],$$

$$D_{13}\binom{q}{12} = D^{*}_{13}\binom{q}{21} = -\frac{\beta}{m}\Big[1 - e^{-2\pi i q_3} + e^{-2\pi i q_2} - e^{-2\pi i q_1}\Big],$$

$$D_{23}\binom{q}{12} = D^{*}_{23}\binom{q}{21} = -\frac{\beta}{m}\Big[1 - e^{-2\pi i q_3} - e^{-2\pi i q_2} + e^{-2\pi i q_1}\Big],$$

.........(3.5)

where $D^*_{\alpha\beta}\binom{q}{kk'}$ is the complex conjugate of $D_{\alpha\beta}\binom{q}{kk'}$.

Since the matrices $D^{\ell}$ are symmetric, the dynamical matrix D(q) in reciprocal space is Hermitian and so all the roots $\omega_j$ of the characteristic equation (1.13) are real.

In the $q_x$, $q_y$, $q_z$ space, the elements of D(q) are:

$$D_{11}\binom{q}{11} = D_{11}\binom{q}{22} = \frac{4}{m}\Big[\alpha + \lambda\{1 - \cos\pi q_y \cos\pi q_z\} + \mu\{2 - \cos\pi q_x \cos\pi q_y - \cos\pi q_z \cos\pi q_x\}\Big],$$

$$D_{22}\binom{q}{11} = D_{22}\binom{q}{22} = \frac{4}{m}\Big[\alpha + \lambda\{1 - \cos\pi q_z \cos\pi q_x\} + \mu\{2 - \cos\pi q_y \cos\pi q_z - \cos\pi q_x \cos\pi q_y\}\Big],$$

$$D_{33}\binom{q}{11} = D_{33}\binom{q}{22} = \frac{4}{m}\Big[\alpha + \lambda\{1 - \cos\pi q_x \cos\pi q_y\} + \mu\{2 - \cos\pi q_z \cos\pi q_x - \cos\pi q_y \cos\pi q_z\}\Big],$$

$$D_{12}\binom{q}{11} = D_{12}\binom{q}{22} = \frac{4\nu}{m}\sin\pi q_x \sin\pi q_y,$$

$$D_{13}\binom{q}{11} = D_{13}\binom{q}{22} = \frac{4\nu}{m}\sin\pi q_z \sin\pi q_x,$$

$$D_{23}\binom{q}{11} = D_{23}\binom{q}{22} = \frac{4\nu}{m}\sin\pi q_y \sin\pi q_z,$$

$$D_{11}\binom{q}{12} = D_{22}\binom{q}{12} = D_{33}\binom{q}{12} = D^*_{11}\binom{q}{21} = D^*_{22}\binom{q}{21} = D^*_{33}\binom{q}{21}$$
$$= -\frac{\alpha}{m}\Big[1 + e^{-\pi i(q_x+q_y)} + e^{-\pi i(q_z+q_x)} + e^{-\pi i(q_y+q_z)}\Big],$$

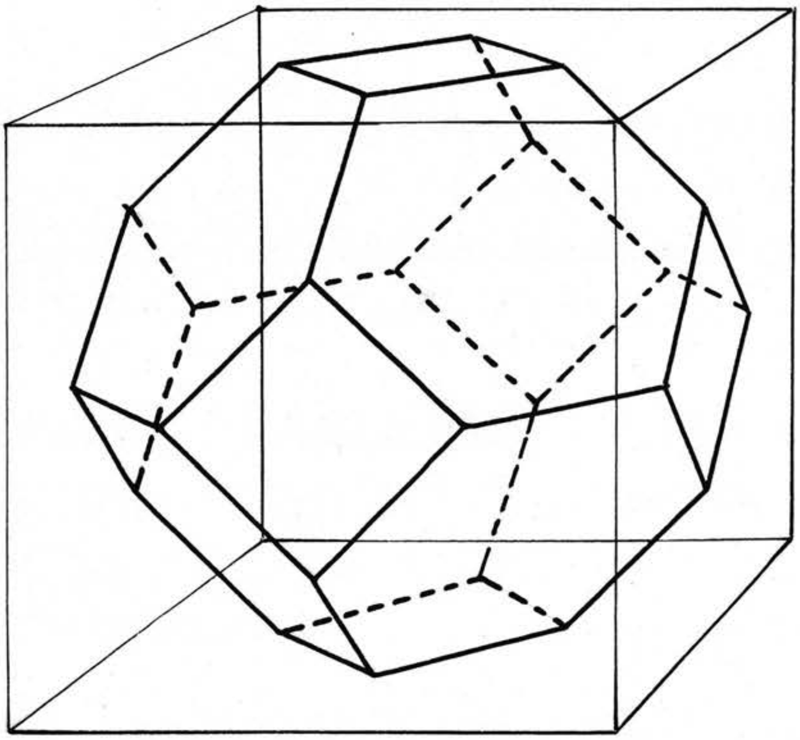
$$D_{12}\binom{q}{12} = D^*_{12}\binom{q}{21} = -\frac{\beta}{m}\Big[1 + e^{-\pi i(q_x+q_y)} - e^{-\pi i(q_z+q_x)} - e^{-\pi i(q_y+q_z)}\Big],$$

$$D_{13}\binom{q}{12} = D^*_{13}\binom{q}{21} = -\frac{\beta}{m}\Big[1 - e^{-\pi i(q_x+q_y)} + e^{-\pi i(q_z+q_x)} - e^{-\pi i(q_y+q_z)}\Big],$$

$$D_{23}\binom{q}{12} = D^*_{23}\binom{q}{21} = -\frac{\beta}{m}\Big[1 - e^{-\pi i(q_x+q_y)} - e^{-\pi i(q_z+q_x)} + e^{-\pi i(q_y+q_z)}\Big].$$

.......(3.6)

FIGURE 3.



THE FIRST BRILLOUIN ZONE OF A FACE-CENTRED CUBIC LATTICE.

(Sommerfeld and Bethe, 1933.)

In order to take full advantage of the symmetry properties of the $D_{\alpha\beta}(q)$ , consider the region of allowed wave-vectors in the $q_x q_y q_z$ space. This is (see fig. 3) the first Brillouin zone of a face-centred lattice, an octahedron with its vertices cut off, defined by

$$\left\{ \begin{array}{l} q_x = \pm 1 : \; q_y = \pm 1 \; : q_z = \pm 1 : \\ q_x \pm q_y \pm q_z = \pm \frac{3}{2} . \end{array} \right. \tag{3.7}$$

Then from the form of the elements $D_{\alpha\beta}(q)$ it is necessary only to consider certain points in the positive octant of the octahedron, points such that

$$\left\{ \begin{array}{l} 0 \le q_z \le q_y \le q_x \le 1 , \\ q_x + q_y + q_z \le \frac{3}{2} . \end{array} \right. \tag{3.8}$$

A selection of points in this positive octant is obtained by dividing the range 0 to 1 of $q_1, q_2, q_3$ into eighths and introducing vector components,

$$p_i = 8 q_i \qquad (p_1, p_2, p_3 \text{ integers}) . \tag{3.9}$$

Then

$$\left\{ \begin{array}{l} q = \frac{\pi}{a} \cdot \frac{1}{8} \left[ (-p_1 + p_2 + p_3), (p_1 - p_2 + p_3), (p_1 + p_2 - p_3) \right] \\ \quad = \frac{\pi}{a} \cdot \frac{1}{8} \left[ p_x , p_y , p_z \right] . \end{array} \right. \tag{3.10}$$

The integers $p_x, p_y, p_z$ are either all odd or all even and

$$\left\{ \begin{array}{l} 0 \le p_z \le p_y \le p_x \le 8 , \\ p_x + p_y + p_z \le 12 . \end{array} \right. \tag{3.11}$$

There are 29 sets of numbers of this type.

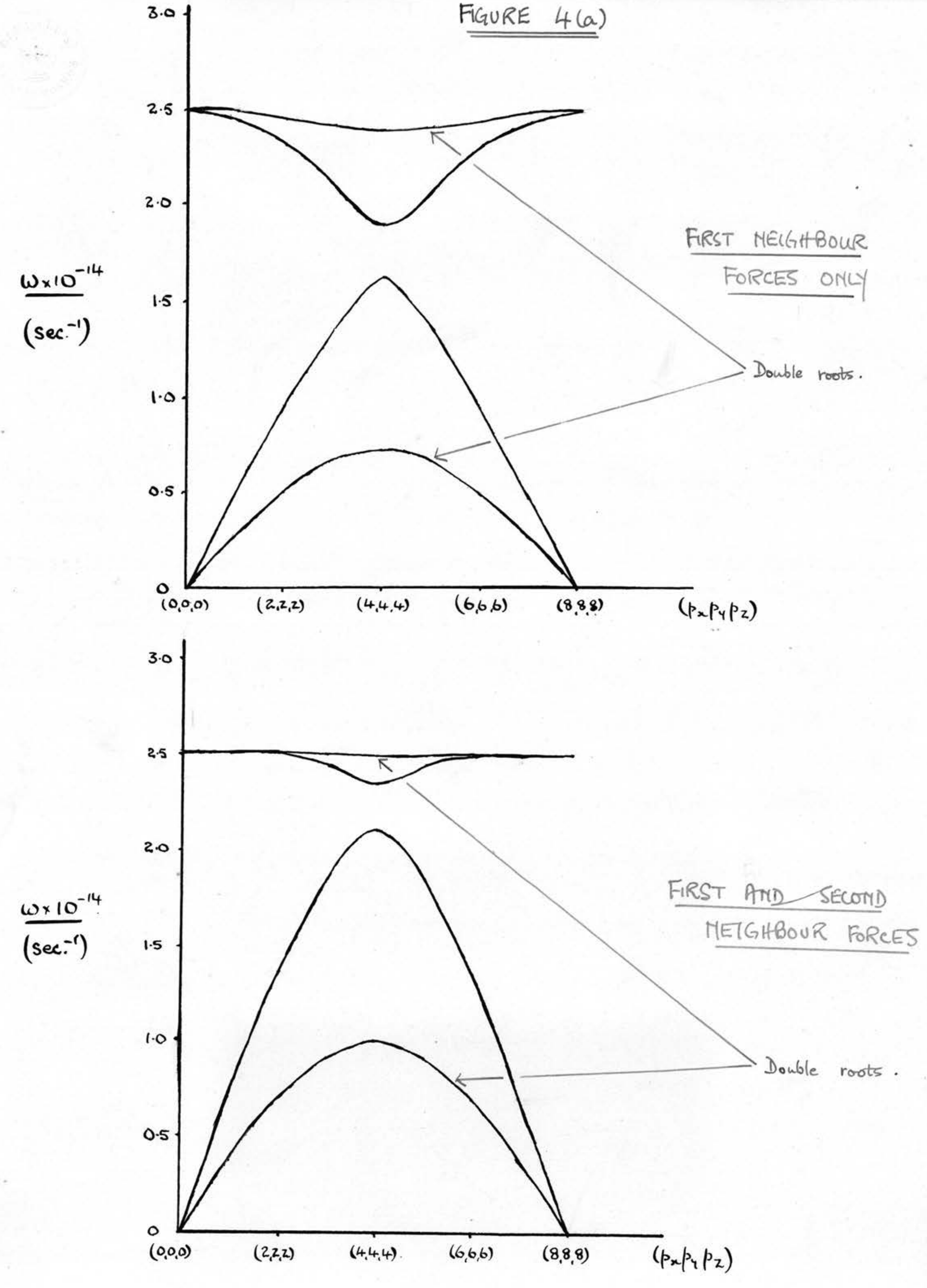
To determine the frequency distribution, the roots of (1.13) for each one of these sets of integers must be weighted according to the number of similar points in the whole octahedron.

$$\text{Let}\quad (3.12)\quad \begin{cases} \lambda = m\omega^2, \\ A = mD_{11}\binom{q}{12} = mD_{22}\binom{q}{12} = mD_{33}\binom{q}{12}, \\ B = mD_{12}\binom{q}{12}, \\ C = mD_{13}\binom{q}{12}, \\ E = mD_{23}\binom{q}{12}, \\ F = mD_{11}\binom{q}{11}, \\ G = mD_{22}\binom{q}{11}, \\ H = mD_{33}\binom{q}{11}, \\ J = mD_{12}\binom{q}{11}, \\ K = mD_{13}\binom{q}{11}, \\ L = mD_{23}\binom{q}{11}, \end{cases}$$

then in the general case, the characteristic equation (1.13) is

$$(3.13)\quad \begin{vmatrix} F-\lambda & J & K & A & B & C \\ J & G-\lambda & L & B & A & E \\ K & L & H-\lambda & C & E & A \\ A^* & B^* & C^* & F-\lambda & J & K \\ B^* & A^* & E^* & J & G-\lambda & L \\ C^* & E^* & A^* & K & L & H-\lambda \end{vmatrix} = 0.$$

FIGURE 4(a)



3.0
2.5
2.0
1.5
1.0
0.5
0
$\omega \times 10^{-14}$
(sec.$^{-1}$)
FIRST NEIGHBOUR FORCES ONLY
Double roots.
(0,0,0)
(2,2,2)
(4,4,4)
(6,6,6)
(8,8,8)
$(p_x p_y p_z)$
3.0
2.5
2.0
1.5
1.0
0.5
0
$\omega \times 10^{-14}$
(sec.$^{-1}$)
FIRST AND SECOND NEIGHBOUR FORCES
Double roots.
(0,0,0)
(2,2,2)
(4,4,4)
(6,6,6)
(8,8,8)
$(p_x p_y p_z)$

A first approximation to the frequency distribution is obtained by neglecting the forces between second neighbours, i.e. put $\lambda = \mu = \nu = 0$.

Then

$$(3.14) \qquad \begin{cases} F = G = H = 4\alpha, \\ J = K = L = 0, \end{cases}$$

and the equation (3.13) reduces to

$$(3.15) \qquad \left| m^2 D\binom{q}{12} . D^*\binom{q}{12} - (4\alpha - \lambda)^2 . I \right| = 0,$$

where I is the unit matrix of order $3 \times 3$.

A second approximation to the frequency distribution is obtained by considering the second neighbour forces to be central forces. Then

$$(2.41) \qquad \begin{cases} \lambda = 0, \\ \mu = \nu . \end{cases}$$

The equation (3.13) has then no general solution and must be solved numerically. However for certain sets of points $(p_x, p_y, p_z)$ the determinant breaks down into determinants of lower order.

(1) : $p_x = p_y = p_z$ or $p_1 = p_2 = p_3$ .

These points lie on the main diagonal of reciprocal space.

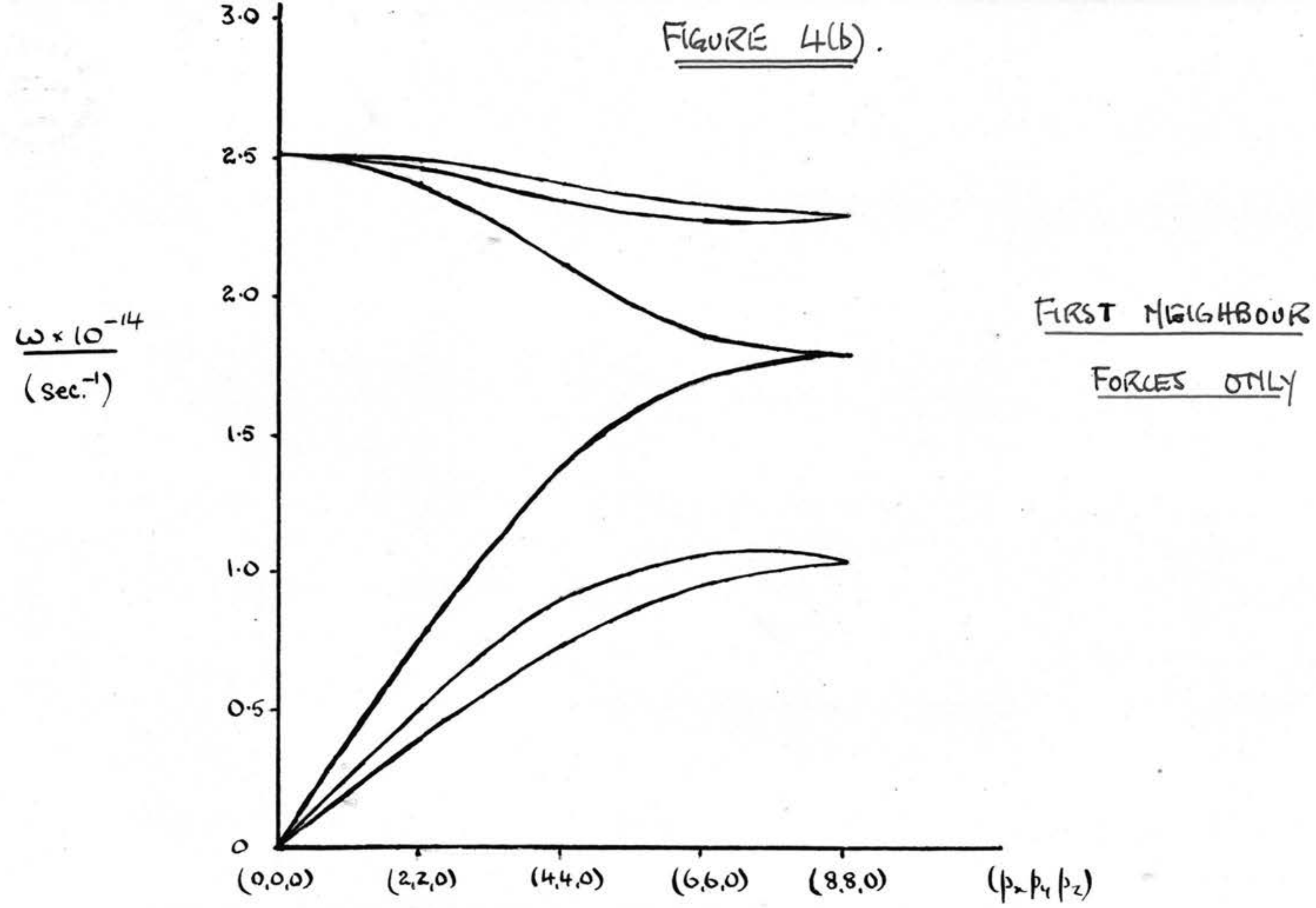
Then from (3.6) and (3.12),

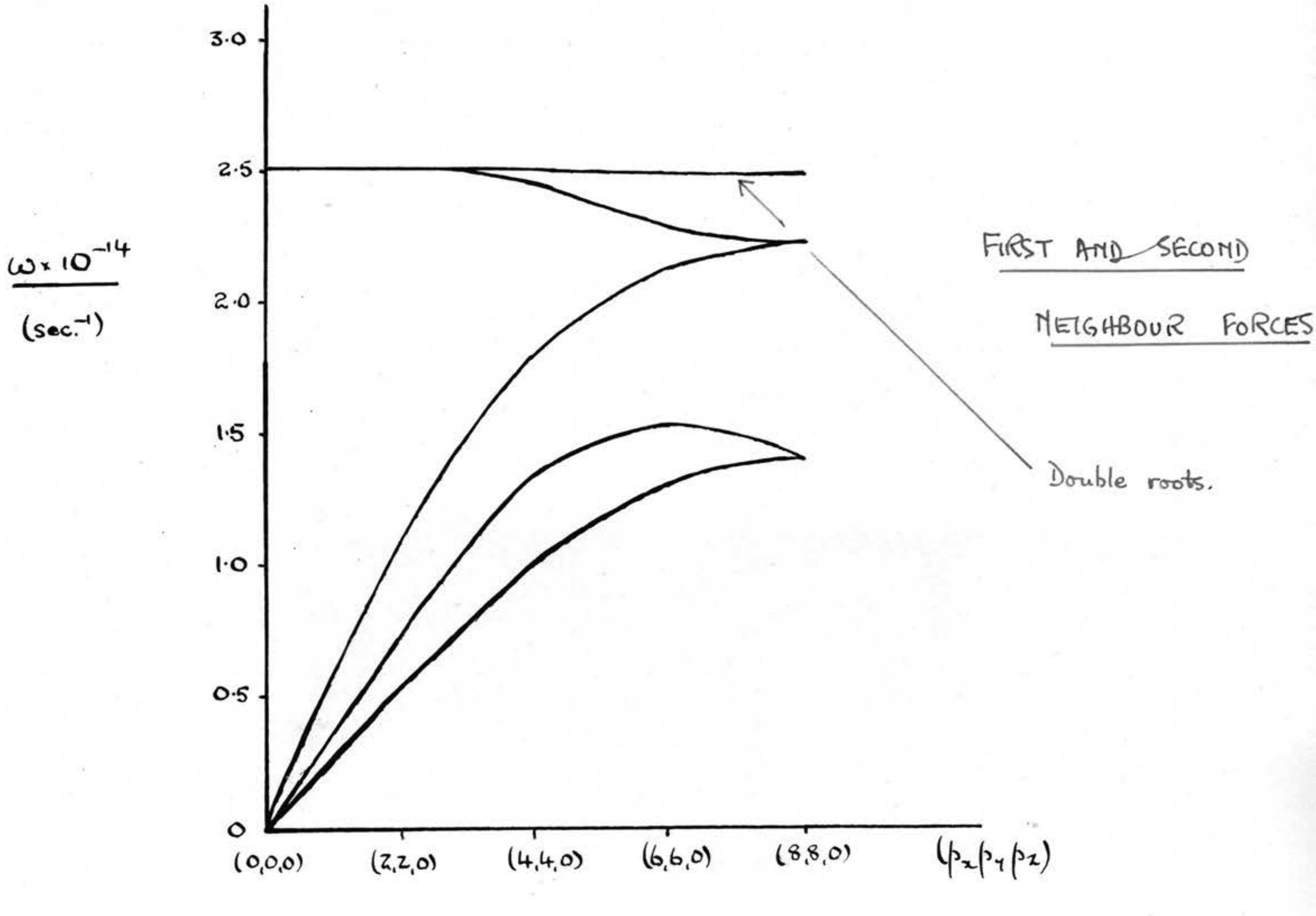
$$(3.16) \qquad \begin{cases} F = G = H, \\ J = K = L, \\ B = C = E . \end{cases}$$

The determinant (3.13) reduces to

$$(3.17) \qquad \begin{vmatrix} F-J-\lambda & A-B \\ A^*-B^* & F-J-\lambda \end{vmatrix}^2 . \begin{vmatrix} F+2J-\lambda & A+2B \\ A^*+2B^* & F+2J-\lambda \end{vmatrix} = 0 .$$

FIGURE 4(b).


3.0
2.5
2.0
1.5
1.0
0.5
0
$\omega \times 10^{-14}$ (sec.$^{-1}$)
(0,0,0)
(2,2,0)
(4,4,0)
(6,6,0)
(8,8,0)
$(p_x p_y p_z)$
FIRST NEIGHBOUR FORCES ONLY


3.0
2.5
2.0
1.5
1.0
0.5
0
$\omega \times 10^{-14}$ (sec.$^{-1}$)
(0,0,0)
(2,2,0)
(4,4,0)
(6,6,0)
(8,8,0)
$(p_x p_y p_z)$
FIRST AND SECOND NEIGHBOUR FORCES
Double roots.

So

$$(3.18)\quad \begin{cases} \lambda_1 = \lambda_2 = 4(\alpha + \mu \sin^2 \pi q_x) \\ \qquad\qquad \pm 2\sqrt{\alpha^2(1+3\cos^2\pi q_x) + \beta(\beta+2\alpha)\sin^2\pi q_x}\,, \\ \lambda_3 = 4(\alpha + 4\mu\sin^2\pi q_x) \\ \qquad\qquad \pm 2\sqrt{\alpha^2(1+3\cos^2\pi q_x) + 4\beta(\beta-\alpha)\sin^2\pi q_x}\,. \end{cases}$$

If $p_x = p_y = p_z = 0$ i.e. $\underline{q} = 0$, then

$$\lambda_1 = \lambda_2 = 4\alpha \pm 2\sqrt{4\alpha^2},$$
$$\lambda_3 = 4\alpha \pm 2\sqrt{4\alpha^2},$$

$$(3.19)\quad \therefore\ \omega_{1,2,3} = \sqrt{\frac{8\alpha}{m}} \quad \text{or} \quad \omega_{4,5,6} = 0\,.$$

This is the frequency shift of the first-order Raman line of diamond; in wave-numbers,

$$(3.20)\qquad \nu = \frac{1}{2\pi c}\sqrt{\frac{8\alpha}{m}}\,,$$

( $c$ = velocity of light ).

(2) : $p_x = p_y : p_z$ arbitrary or $p_1 = p_2 : p_3$ arbitrary.

This gives

$$(3.21)\qquad C = E\ ;\ F = G\ ;\ K = L\,.$$

The determinant (3.13) splits into a determinant of the fourth order and one of the second order.

If in addition $p_z = 0$, then $K = L = 0$, but no further simplification of the determinant results.

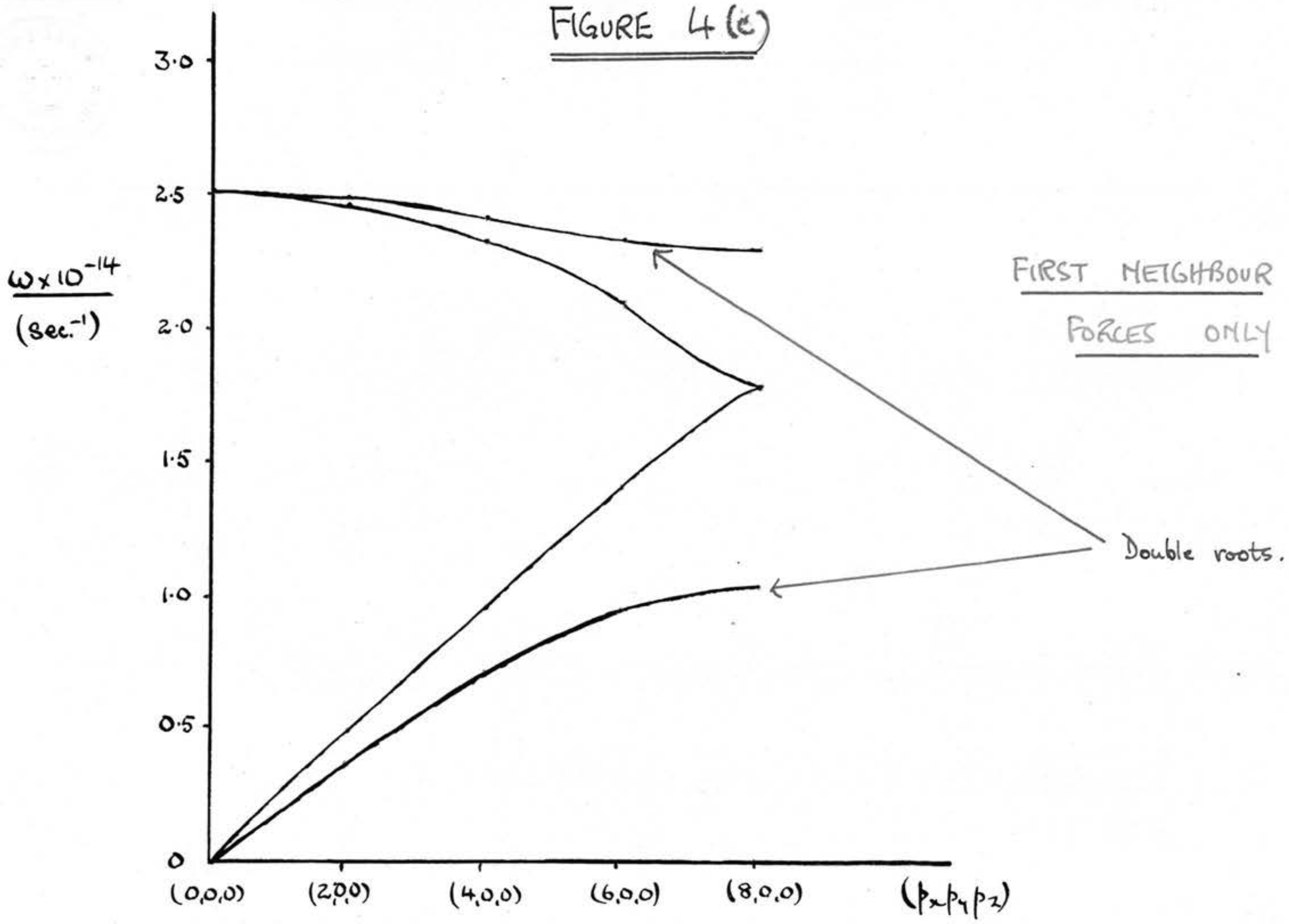
(3) : $p_x$ arbitrary : $p_y = p_z$ or $p_1$ arbitrary : $p_2 = p_3$.

Then

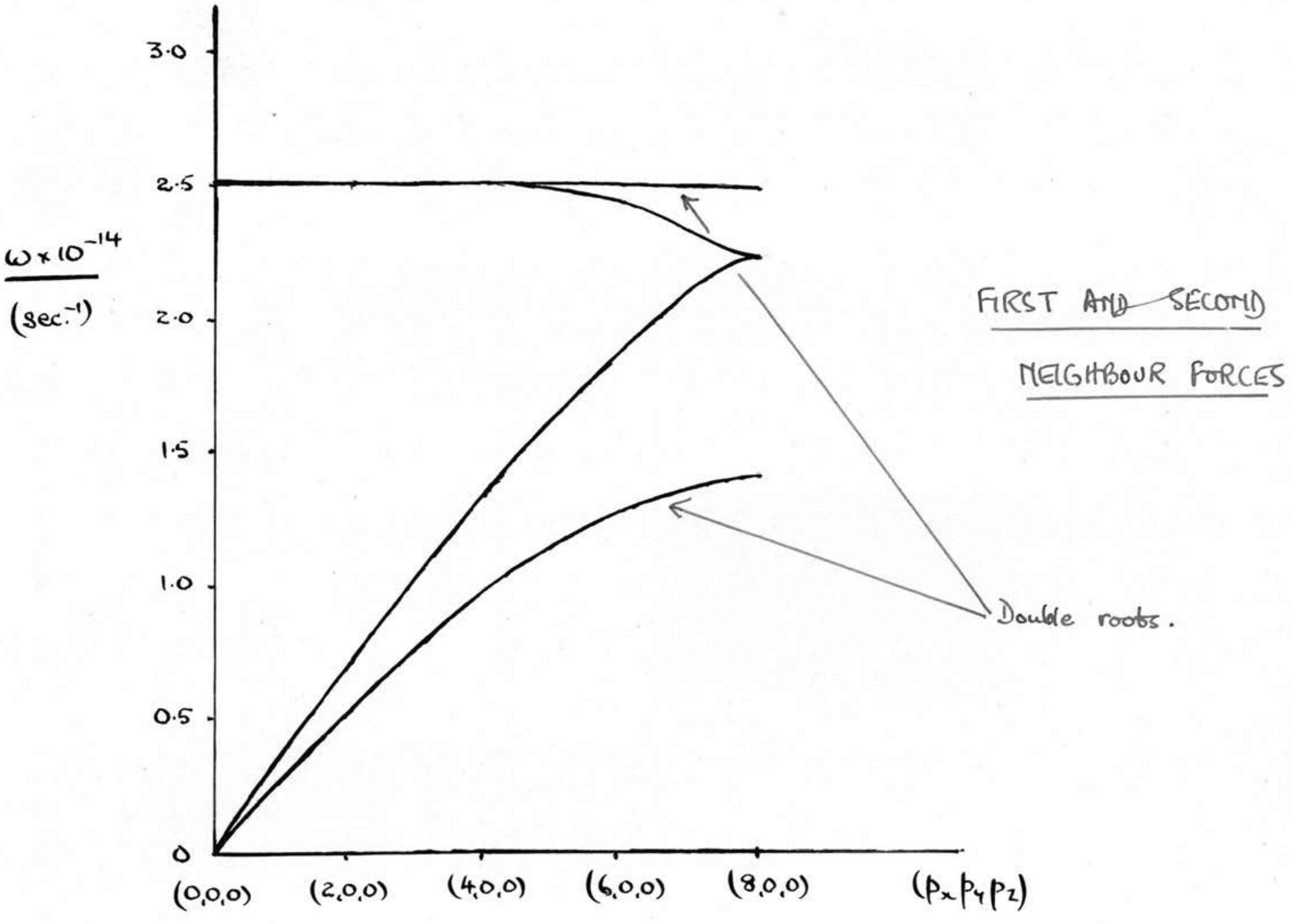
$$(3.22)\qquad B = C\ ;\ G = H\ ;\ J = K\,.$$

As in (2), the determinant splits into two smaller determinants, one of the fourth order and one of the second order.

FIGURE 4 (c)



3.0
2.5
2.0
1.5
1.0
0.5
0
ω x 10^-14
(sec.^-1)
(0,0,0)
(2,0,0)
(4,0,0)
(6,0,0)
(8,0,0)
(px py pz)
FIRST NEIGHBOUR
FORCES ONLY
Double roots.

3.0
2.5
2.0
1.5
1.0
0.5
0
ω x 10^-14
(sec.^-1)
(0,0,0)
(2,0,0)
(4,0,0)
(6,0,0)
(8,0,0)
(px py pz)
FIRST AND SECOND
NEIGHBOUR FORCES
Double roots.

If, in addition, $p_y = p_z = 0$ i.e. $p_1 = 0$, $p_2 = p_3$,

(3.23) $$B = C = 0 : \quad J = K = L = 0 .$$

Then

(3.24) $$\begin{vmatrix} G-\lambda & A+E \\ A^*+E^* & G-\lambda \end{vmatrix} \cdot \begin{vmatrix} G-\lambda & A-E \\ A^*-E^* & G-\lambda \end{vmatrix} \cdot \begin{vmatrix} F-\lambda & A \\ A^* & F-\lambda \end{vmatrix} = 0 .$$

Since $(A+E)(A^*+E^*) = (A-E)(A^*-E^*)$,

(3.25) $$\begin{cases} \lambda_1 = \lambda_2 = 4\alpha + 4\mu(1-\cos\pi q_x) \\ \qquad\qquad + 2\sqrt{2}\sqrt{\alpha^2+\beta^2+(\alpha^2-\beta^2)\cos\pi q_x} , \\ \lambda_3 = 4\alpha + 8\mu(1-\cos\pi q_x) \\ \qquad\qquad \pm 2\sqrt{2}\,\alpha\sqrt{1+\cos\pi q_x} . \end{cases}$$

(4) : $p_x = 8 : p_y : p_z = 0$ .

Then

(3.26) $$A = C = J = K = L = 0 ,$$

and (3.13) becomes

(3.27) $$\left[(F-\lambda)(G-\lambda)(H-\lambda) - EE^*(F-\lambda) - BB^*(H-\lambda)\right]^2 = 0 .$$

(5) : $p_x \neq p_y \neq p_z$ .

The roots of (3.13) have been calculated numerically by a method due to Aitken (1937).

## 4. NUMERICAL RESULTS.

There are four quantities expressed in terms of the three parameters $\alpha$, $\beta$, $\mu$ : these are the elastic constants

$$(2.42)\qquad \begin{cases} c_{11} = \frac{1}{2a}(\alpha + 8\mu), \\ c_{44} = \frac{1}{2a}\left(\alpha - \frac{\beta^2}{\alpha} + 4\mu\right), \\ c_{12} = \frac{1}{2a}(2\beta - \alpha + 4\mu), \end{cases}$$

and the frequency shift of the first-order Raman line,

$$(3.20)\qquad \nu = \frac{1}{2\pi c}\sqrt{\frac{8\alpha}{m}}\ .$$

There is an identity between these four quantities :

$$(4.1)\qquad \frac{8.\,4\pi^2c^2.\frac{m}{2a}.\nu^2\left[4\pi^2c^2.\frac{m}{2a}.\nu^2 + 8c_{11} - 16c_{44}\right]}{\left[3.\,4\pi^2c^2.\frac{m}{2a}.\nu^2 - 8c_{11} + 16c_{12}\right]^2} = 1\,.$$

If the action of second neighbours is neglected ($\mu = 0$), (4.1) breaks up into two identities,

$$(2.31)\qquad \frac{4c_{11}(c_{11} - c_{44})}{(c_{11} + c_{12})^2} = 1,$$

which has been obtained already in Section 2, and

$$(4.2)\qquad \frac{4\pi^2c^2.\frac{m}{2a}.\nu^2}{8c_{11}} = 1\,.$$

The frequency shift of the first-order Raman line of diamond is

$$(4.3)\qquad \nu = 1332\ \text{cm}^{-1}$$

(see, for example, Robertson, Fox & Martin (1934) ).

The only direct measurements of the elastic constants of diamond are those of Bhagavantam & Bhimasenachar (1946) : they obtained the values

$$(4.4)\qquad \left.\begin{aligned} c_{11} &= 9.5 \times 10^{12} \\ c_{44} &= 4.3 \times 10^{12} \\ c_{12} &= 3.9 \times 10^{12} \end{aligned}\right\} \quad \text{dynes/cm.}^2$$

Adams (1921) and Williamson (1922) have determined the compressibility of diamond, both using the same apparatus. They found, respectively, 0.16 and $0.18\times10^{-6}$ per megabar: the mean of these results, $0.17\times10^{-6}$ per megabar, corresponds to a bulk-modulus

$$(4.5)\qquad 5.9 \times 10^{12} \text{ dynes/cm.}^2.$$

But the bulk-modulus

$$(4.6)\qquad \frac{1}{K} = \frac{1}{3}\left(c_{11} + 2c_{12}\right),$$

and substitution of the values (4.4) gives

$$(4.7)\qquad \frac{1}{K} = 5.8 \times 10^{12} \text{ dynes/cm.}^2,$$

in reasonable agreement with (4.5).

Now substituting the experimental values (4.3) and (4.4) in the identities (4.1), (2.31), (4.2), taking the lattice constant

$$(4.8)\qquad \left\{\begin{aligned} 2a &= 3.56 \times 10^{-8} \text{ cm.}, \\ m &= 1.995\times10^{-23} \text{ gm.}, \\ c &= 3 \times 10^{10} \text{ cm/sec.}, \end{aligned}\right.$$

we find

$$(4.9)\qquad \text{L. H. S. of } (4.1) = 1.40,$$

$$(4.10)\qquad \text{L. H. S. of } (2.31) = 1.10,$$

$$(4.11)\qquad \text{L. H. S. of } (4.2) = 0.46.$$

The discrepancies (4.10) and (4.11) show that the action of first neighbour forces is not sufficient to explain the physical properties of diamond, but (4.9), which takes into account second neighbour forces, though an improvement on (4.11), is worse than (4.10). As Born (1946) has already pointed out, there are three possible explanations, either there are experimental errors, or the second neighbour forces are not central, or more distant neighbours exert appreciable forces. Acceptance of the second or third alternative would preclude, at present, any determination of numerical values of $\alpha$, $\beta$, $\mu$. Moreover, in view of the agreement between the two values of the bulk-modulus (4.5) and (4.7), experimental errors in $c_{11}$ and $c_{12}$ must be small.

Since the Raman frequency shift (4.3) is measured optically and so to greater accuracy than the elastic constants, from (3.20) and (4.3),

$$(4.12) \qquad \alpha = \frac{4\pi^2 c^2 m \nu^2}{8} = 0.157 \times 10^6 \quad \text{dynes/cm..}$$

Then $\alpha + 8\mu = 2ac_{11}$, so from (4.4) and (4.12),

$$(4.13) \qquad \mu = 0.0226 \times 10^6 \quad \text{dynes/cm.,}$$

and

$$\frac{1}{k} = \frac{1}{3}(c_{11} + 2c_{12}) = \frac{1}{6a}(4\beta - \alpha + 16\mu),$$

giving, from (4.7), (4.12), (4.13),

$$(4.14) \qquad \beta = 0.104 \times 10^6 \quad \text{dynes/cm..}$$

Now $$c_{44} = \frac{1}{2a}\left(\alpha - \frac{\beta^2}{\alpha} + 4\mu\right)$$

(4.15) $$= 5.0\times10^{12} \text{ dynes/cm.}^2$$

on substitution of the values (4.12), (4.13), (4.14).

Lastly the observed values

$$\nu = 1332 \text{ cm.}^{-1},$$

$$c_{11} = 9.5\times10^{12} \text{ dynes/cm.}^2,$$

$$c_{12} = 3.9\times10^{12} \text{ dynes/cm.}^2,$$

and the calculated value

$$c_{44} = 5.0\times10^{12} \text{ dynes/cm.}^2,$$

give

(4.16) $$\begin{cases} \text{L. H. S. of } (4.1) = 1.04, \\ \text{L. H. S. of } (2.31) = 0.95. \end{cases}$$

Thus a change in the value of $c_{44}$ from 4.3 to $5.0\times10^{12}$ dynes/cm.$^2$ considerably improves the value of the identity (4.1).

Numerical values of elements of mD(q) for the 29 sets of integers $p_x, p_y, p_z$, given by (3.11), are obtained from (3.6) using the values (4.12), (4.13), (4.14) of $\alpha$, $\beta$, and $\mu$.

Table 6 gives the numerical values of the frequencies of vibration $\omega_j$ for these 29 points considering forces between first neighbours only. Table 7 gives numerical values of frequencies if, in addition, there are central forces between second neighbours in the lattice.

# Table 6.

## Frequencies of vibration of diamond under the action of first neighbour forces only.

(Units of $\omega_j$ are $10^{14}$ sec.$^{-1}$ : to convert to wave-numbers, multiply by $\frac{1}{2\pi c} = 0.0531 \times 10^{-10}$.)

| | ← Optical branches | → | ← Acoustic branches | | | → |
|---|---|---|---|---|---|---|
| $p_x\ p_y\ p_z$ | $\omega_1$ | $\omega_2$ | $\omega_3$ | $\omega_4$ | $\omega_5$ | $\omega_6$ |
| 8 4 0 | 2.29 | 2.29 | 1.78 | 1.78 | 1.03 | 1.03 |
| 8 2 2 | 2.32 | 2.27 | 1.84 | 1.71 | 1.06 | 0.95 |
| 8 2 0 | 2.29 | 2.29 | 1.78 | 1.78 | 1.03 | 1.03 |
| 8 0 0 | 2.29 | 2.29 | 1.78 | 1.78 | 1.03 | 1.03 |
| 7 3 1 | 2.33 | 2.28 | 1.89 | 1.66 | 1.05 | 0.95 |
| 7 1 1 | 2.31 | 2.30 | 1.93 | 1.61 | 1.02 | 0.99 |
| 6 6 0 | 2.32 | 2.27 | 1.84 | 1.71 | 1.06 | 0.95 |
| 6 4 2 | 2.36 | 2.33 | 1.92 | 1.62 | 0.94 | 0.85 |
| 6 4 0 | 2.35 | 2.29 | 1.94 | 1.59 | 1.03 | 0.90 |
| 6 2 2 | 2.35 | 2.33 | 1.98 | 1.54 | 0.94 | 0.88 |
| 6 2 0 | 2.34 | 2.32 | 2.04 | 1.46 | 0.97 | 0.91 |
| 6 0 0 | 2.33 | 2.33 | 2.09 | 1.40 | 0.94 | 0.94 |
| 5 5 1 | 2.37 | 2.31 | 1.94 | 1.60 | 0.98 | 0.85 |
| 5 3 3 | 2.39 | 2.38 | 1.95 | 1.58 | 0.80 | 0.78 |
| 5 3 1 | 2.38 | 2.35 | 2.07 | 1.42 | 0.89 | 0.79 |
| 5 1 1 | 2.37 | 2.37 | 2.18 | 1.25 | 0.83 | 0.82 |
| 4 4 4 | 2.40 | 2.40 | 1.91 | 1.63 | 0.73 | 0.73 |
| 4 4 2 | 2.40 | 2.38 | 2.02 | 1.49 | 0.81 | 0.73 |
| 4 4 0 | 2.40 | 2.34 | 2.11 | 1.37 | 0.90 | 0.73 |
| 4 2 2 | 2.41 | 2.41 | 2.17 | 1.26 | 0.71 | 0.69 |
| 4 2 0 | 2.43 | 2.38 | 2.25 | 1.11 | 0.79 | 0.65 |
| 4 0 0 | 2.41 | 2.41 | 2.32 | 0.96 | 0.70 | 0.70 |
| 3 3 3 | 2.42 | 2.42 | 2.11 | 1.36 | 0.67 | 0.67 |
| 3 3 1 | 2.44 | 2.41 | 2.24 | 1.13 | 0.70 | 0.59 |
| 3 1 1 | 2.46 | 2.45 | 2.36 | 0.86 | 0.55 | 0.52 |
| 2 2 2 | 2.46 | 2.46 | 2.33 | 0.95 | 0.50 | 0.50 |
| 2 2 0 | 2.48 | 2.46 | 2.40 | 0.75 | 0.50 | 0.39 |
| 2 0 0 | 2.48 | 2.48 | 2.46 | 0.49 | 0.37 | 0.37 |
| 1 1 1 | 2.50 | 2.50 | 2.46 | 0.48 | 0.27 | 0.27 |

## Table 7.

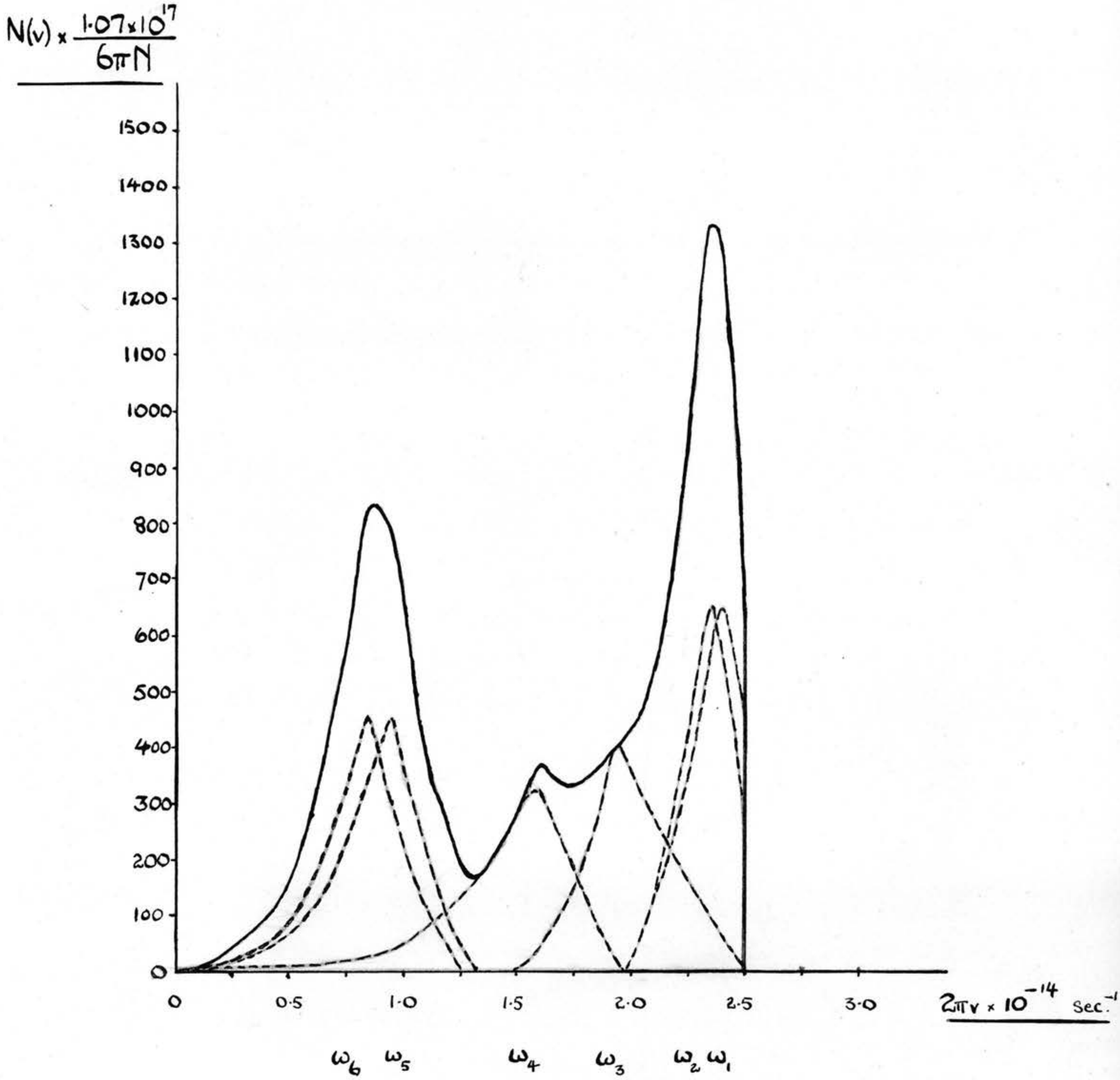
**Frequencies of vibration of diamond under the action of first and second neighbour forces.**

(Units of $\omega_j$ are $10^{14}$ sec.$^{-1}$: to convert to wave-numbers, multiply by $\frac{1}{2\pi c} = 0.0531 \times 10^{-10}$.)

← Optical branches → ← Acoustic branches →

| $p_x$ $p_y$ $p_z$ | $\omega_1$ | $\omega_2$ | $\omega_3$ | $\omega_4$ | $\omega_5$ | $\omega_6$ |
|---|---|---|---|---|---|---|
| 8 4 0 | 2.51 | 2.51 | 2.12 | 2.12 | 1.48 | 1.48 |
| 8 2 2 | 2.48 | 2.48 | 2.27 | 2.12 | 1.53 | 1.30 |
| 8 2 0 | 2.51 | 2.51 | 2.17 | 2.17 | 1.44 | 1.44 |
| 8 0 0 | 2.48 | 2.48 | 2.23 | 2.23 | 1.40 | 1.40 |
| 7 3 1 | 2.50 | 2.50 | 2.24 | 2.07 | 1.55 | 1.33 |
| 7 1 1 | 2.48 | 2.48 | 2.30 | 2.06 | 1.43 | 1.35 |
| 6 6 0 | 2.48 | 2.48 | 2.27 | 2.12 | 1.53 | 1.30 |
| 6 4 2 | 2.51 | 2.51 | 2.28 | 2.07 | 1.35 | 1.16 |
| 6 4 0 | 2.51 | 2.51 | 2.34 | 2.01 | 1.47 | 1.25 |
| 6 2 2 | 2.49 | 2.49 | 2.33 | 1.96 | 1.37 | 1.21 |
| 6 2 0 | 2.51 | 2.51 | 2.40 | 1.90 | 1.34 | 1.23 |
| 6 0 0 | 2.49 | 2.49 | 2.43 | 1.87 | 1.28 | 1.28 |
| 5 5 1 | 2.49 | 2.49 | 2.27 | 2.00 | 1.46 | 1.15 |
| 5 3 3 | 2.49 | 2.49 | 2.32 | 2.06 | 1.13 | 1.06 |
| 5 3 1 | 2.51 | 2.51 | 2.35 | 1.88 | 1.30 | 1.05 |
| 5 1 1 | 2.50 | 2.50 | 2.42 | 1.68 | 1.17 | 1.14 |
| 4 4 4 | 2.50 | 2.50 | 2.34 | 2.11 | 0.99 | 0.99 |
| 4 4 2 | 2.50 | 2.50 | 2.38 | 1.96 | 1.14 | 0.99 |
| 4 4 0 | 2.50 | 2.50 | 2.44 | 1.78 | 1.33 | 0.99 |
| 4 2 2 | 2.50 | 2.49 | 2.49 | 1.71 | 0.98 | 0.98 |
| 4 2 0 | 2.51 | 2.51 | 2.49 | 1.54 | 1.09 | 0.88 |
| 4 0 0 | 2.51 | 2.51 | 2.51 | 1.35 | 0.97 | 0.97 |
| 3 3 3 | 2.50 | 2.50 | 2.45 | 1.84 | 0.91 | 0.91 |
| 3 3 1 | 2.50 | 2.50 | 2.43 | 1.55 | 1.01 | 0.80 |
| 3 1 1 | 2.51 | 2.51 | 2.51 | 1.21 | 0.77 | 0.74 |
| 2 2 2 | 2.51 | 2.51 | 2.51 | 1.34 | 0.69 | 0.69 |
| 2 2 0 | 2.51 | 2.51 | 2.51 | 1.07 | 0.73 | 0.54 |
| 2 0 0 | 2.51 | 2.51 | 2.51 | 0.71 | 0.52 | 0.52 |
| 1 1 1 | 2.51 | 2.51 | 2.51 | 0.71 | 0.37 | 0.37 |

FIGURE 5




FREQUENCY DISTRIBUTION OF DIAMOND

(FIRST NEIGHBOUR FORCES ONLY).

The frequencies belonging to certain wave-vectors have been plotted in fig. 4 : the wave-vectors are given in terms of $p_x, p_y, p_z$ . The separation into optical and acoustic branches is obvious. The degeneracies in some of the graphs could be removed by a more accurate determination of the values of $\alpha$ , $\beta$ and $\mu$ than was possible from the available experimental data.

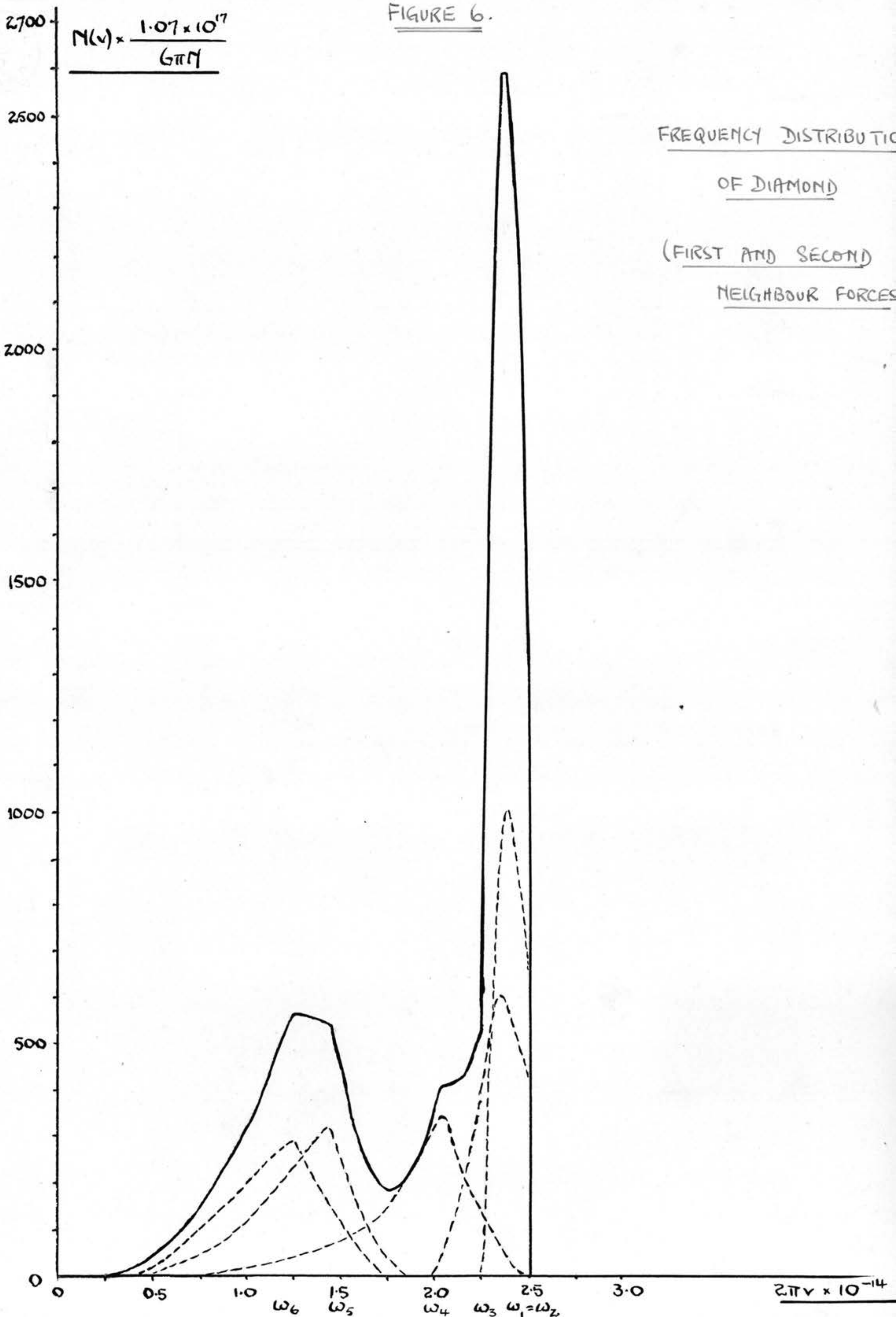
The frequency spectrum $N(\nu)$ can be derived from the calculated frequencies by dividing the range of values of $\nu$ into equal intervals $d\nu$ and counting the number of frequencies in each interval. Having regard to the accuracy of the calculations and the total number of frequencies, the interval chosen was $d\omega = 2\pi d\nu = 0.3 \times 10^{14}$ $\text{sec}^{-1}$.
Thus three histograms were plotted, each shifted $0.1 \times 10^{14}$ in the $\omega$ scale from the other two. These histograms were then smoothed out and gave the frequency distribution curves shown (figs. 5 and 6) which were normalised so that

$$\int_0^\infty N(\nu)\,d\nu = 3N , \tag{4.17}$$

where $N(\nu)$ is the number of frequencies in the interval $\nu$ to $\nu+d\nu$ and $N$ is Avogadro's number.

Separate distribution curves were drawn for the six branches of the spectra: these are also shown in figs. 5 and 6.

FIGURE 6.



$N(\nu) \times \frac{1.07 \times 10^{17}}{6\pi N}$
FREQUENCY DISTRIBUTIO
OF DIAMOND
(FIRST AND SECOND
NEIGHBOUR FORCES
2700
2500
2000
1500
1000
500
0
0
0.5
1.0
1.5
2.0
2.5
3.0
$2\pi\nu \times 10^{-14}$
$\omega_6$
$\omega_5$
$\omega_4$
$\omega_3$
$\omega_1 = \omega_2$

Comparison of Tables 6 and 7 and figs. 5 and 6 shows that the introduction of second neighbour central forces increases the magnitude of the calculated frequencies for all the 29 points of reciprocal space chosen.

The main features of the two frequency distributions are given in Table 8.

Table 8.

| | Fig. 5 (First Neighbour Forces Only) | Fig. 6 (First + Second Neighbour Forces) |
|---|---|---|
| Frequency of main maximum. | $\omega_1 = 2.35 \times 10^{14}$ sec.$^{-1}$ | $\omega_1 = 2.40 \times 10^{14}$ sec.$^{-1}$ |
| " of second maximum. | $\omega_2 = 0.87 \times 10^{14}$ sec.$^{-1}$ | $\omega_2 = 1.25 \times 10^{14}$ sec.$^{-1}$ |
| " of minimum. | $\omega_3 = 1.32 \times 10^{14}$ sec.$^{-1}$ | $\omega_3 = 1.75 \times 10^{14}$ sec.$^{-1}$ |
| $\omega_1 : \omega_2$ | 2.7 | 1.9 |
| $\omega_1 : \omega_3$ | 1.8 | 1.4 |
| $\frac{\text{Ht. of main max.}}{\text{Ht. of second max.}}$ | 1.6 | 4.6 |
| $\frac{\text{Ht. of main max.}}{\text{Ht. of minimum}}$ | 7.8 | 14.4 |

The shape of the frequency distribution resembles closely that calculated by Blackman (1937) for a simple cubic lattice containing one type of particle.

## 5. SPECIFIC HEAT OF DIAMOND.

If $N(\nu)$ is the frequency distribution function of a crystal then the specific heat at constant volume of 1 mole is

$$C_v = k\int_0^\infty N(\nu).E\left(\frac{h\nu}{kT}\right) d\nu, \tag{5.1}$$

where $k$ = Boltzmann's constant,

$h$ = Planck's constant,

$T$ = absolute temperature,

$E(x) = \dfrac{x^2 e^x}{(e^x-1)^2}$ is the Einstein function.

$N(\nu)$ is normalised so that its integral over the entire spectrum gives the total number of frequencies per mole, i.e. in the case of diamond,

$$\int_0^\infty N(\nu)d\nu = 3N. \tag{4.17}$$

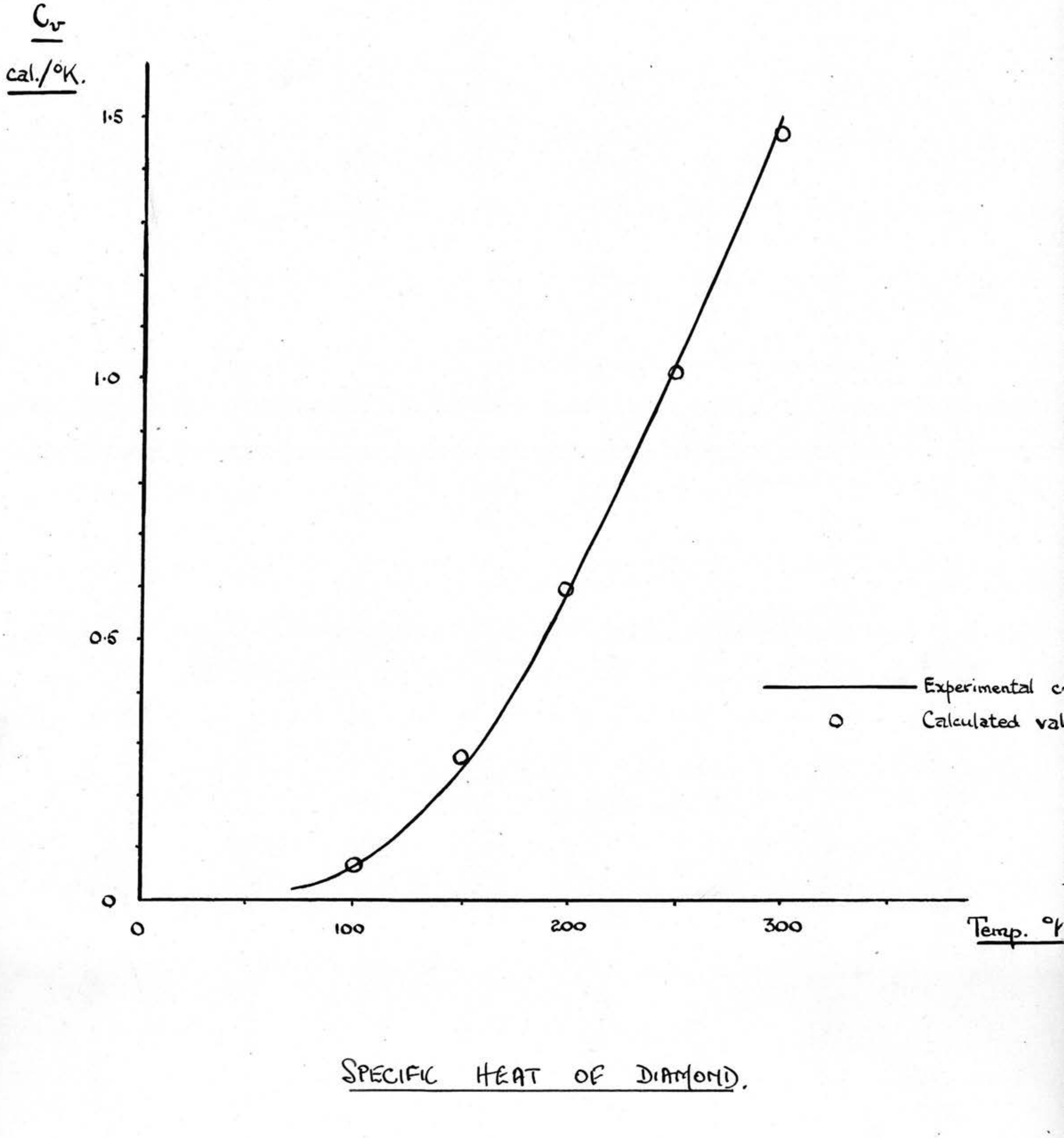
The Einstein function has been tabulated (Landolt-Bornstein (1927) ); values of $N(\nu)$ were taken from figs. 5 and 6 and the function $N(\nu).E\left(\frac{h\nu}{kT}\right)$ was integrated numerically for various values of T.

Using the distribution function for first neighbour forces only (fig. 5),

$$\begin{cases} C_v = 0.240 \text{ cal./}^\circ\text{K at } T = 100^\circ\text{K.} \\ C_v = 1.159 \text{ cal./}^\circ\text{K at } T = 200^\circ\text{K.} \end{cases} \tag{5.2}$$

The results obtained using the distribution function (fig. 6) for first and second neighbour forces are given in Table 9 together with the values of the characteristic temperature $\Theta$ derived from the specific heat according to Debye's theory.

FIGURE 7.




SPECIFIC HEAT OF DIAMOND.

Table 9.

| Temperature °K. | $C_v$ cal./°K. | $\Theta$ °K. |
|---|---|---|
| 100 | 0.0669 | 1910 |
| 150 | 0.270 | 1800 |
| 200 | 0.596 | 1810 |
| 250 | 1.009 | 1840 |
| 300 | 1.463 | 1870 |
| 400 | 2.360 | 1910 |
| 500 | 3.139 | 1920 |
| 1000 | 4.957 | 1960 |
| 1200 | 5.231 | 1960 |

Born & v. Kármán (1912) have shown that the characteristic temperature $\Theta$ at zero absolute temperature is

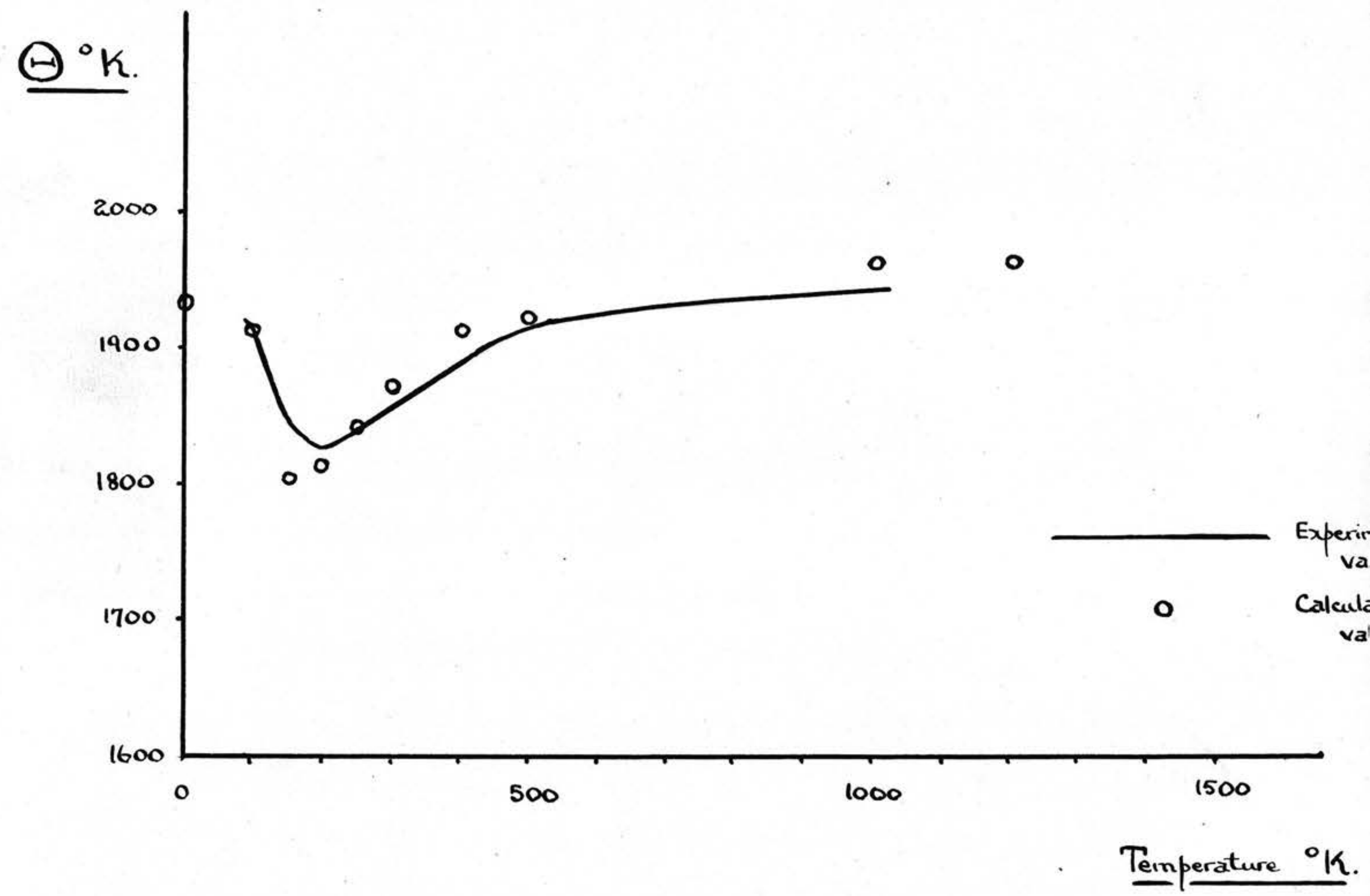
(5.3) $$\Theta = \frac{h}{k}\left(\frac{3}{4\pi\Omega}\right)^{\frac{1}{3}}\bar{v},$$

where $\Omega$ is the atomic volume and $\bar{v}$ the mean velocity of propagation of waves in the crystal. $\bar{v}$ can be calculated from the elastic constants of the crystal by an approximation given by Hopf & Lechner (1914). For diamond, this gives

(5.4) $$\Theta = 1930\,°K.,$$

at zero absolute temperature.

FIGURE 8.




TEMPERATURE DEPENDENCE OF Θ.

Experimental values of the specific heat of diamond have been obtained by Nernst (1911), Magnus & Hodler (1926), Robertson, Fox & Martin (1936), and Pitzer (1938). The curve obtained from the experimental data for temperatures between 70°K. and 300°K. is given in fig. 7. Comparing the calculated specific heats (5.2) and Table 9 with experiment, it is evident that although first neighbour forces alone give far from accurate results, the introduction of second neighbour central forces produces values of the specific heat in close agreement with experiment. Fig. 8 shows the relation between experimental and theoretical values of the characteristic temperature $\Theta$ and illustrates the deviation from Debye's theory.

There is no information available on the temperature variation of the measured elastic constants, but Krishnan (1946a and b) has investigated the thermal expansion of diamond and the temperature variation of the Raman frequencies. The frequency shift of the principal Raman line decreases from 1333.2 $cm.^{-1}$ at 85°K. to 1316 $cm.^{-1}$ at 976°K., i.e. a variation of 1.3% per 900°K. of the value at 300°K.. The corresponding change in the atomic constant $\alpha$ over 900°K. is, from (4.12), approximately 2½% of the value at 300°K.. Since the variation in the lattice constant is only about 1/5 % per 900°K., the change in the elastic constants can be taken to be $2\frac{1}{2}\%$ per $900^{\circ}$K., i.e. 1/3 % per $100^{\circ}$K. of the value at room temperature. This variation will have no appreciable effect on the calculated specific heats as it is much less than the limit of error of the calculations.

# PART II.

## THE RAMAN SPECTRUM OF DIAMOND.

### 6. INTRODUCTION.

The Raman effect, the scattering of light by liquids and crystals with change in frequency, was first observed in 1928. In the case of crystals, the frequency differences between the incident and the scattered light can be correlated with the vibrational energy states. To simplify the problem, Placzek (1934) assumed that though it is the electrons which interact with the incident radiation, the changes in energy are absorbed by the nuclei which perform small harmonic oscillations about fixed positions. The polarisability tensor of the crystal, on which depends the induced electric moment, can then be expressed as a power-series in the vibrational amplitudes, and so the matrix elements of the polarisability are calculated in terms of the energy states of the nuclei and the unperturbed electric moment of the crystal.

The Raman spectrum of diamond has been investigated since 1930, but before 1944 only a single intense line with a frequency shift of 1332 $cm.^{-1}$ had been observed, (e.g. Robertson, Fox & Martin (1934)). This line was attributed to the triply degenerate vibration against each other of the two inter-penetrating simple lattices of carbon atoms. In 1944

Krishnan succeeded in photographing the second-order Raman spectrum of diamond using the 2536 Å. radiation from a water-cooled quartz mercury arc. He repeated his observations in 1946, obtaining spectra of greater intensity and higher resolution. This experimental method, first developed by Rasetti in 1930, can be used only with ultra-violet transparent diamonds, but since both ultra-violet transparent and ultra-violet opaque diamonds give the same frequency shift for the principal Raman line, it is unlikely that there is any difference between the second-order spectra of the two types. The second-order spectrum consists of a continuous band with super-imposed small peaks, extending over about 600 $cm.^{-1}$ with its maximum near the mercury line at 2698.9 Å.. The frequency shift of this maximum from the exciting line is 2460 $cm.^{-1}$. There is a small peak with a shift of 2176 $cm.^{-1}$ at the high frequency side of the band, and at the other side a sharp line at 2666 $cm.^{-1}$ (the octave of the first-order frequency) marks the cut-off of the band.

The Raman spectrum of any crystal consists in general of a first-order line spectrum, a second-order line spectrum of sums and differences of the first-order frequency shifts, and a second-order continuous spectrum of sums and differences of any two vibration frequencies belonging to the same wave-vector. Born & Bradburn (1947) first developed the theory of the second-order continuous spectrum and applied their results quantitatively to rocksalt. The general theory explains satisfactorily the main features of the diamond spectrum, the extent of the continuous band and the positions of the maxima and the cut-off. The results depend only on the measured elastic constants, the lattice constant and the first-order Raman frequency shift. In order to explain the relative intensities of the different maxima it would be necessary to consider the interaction between electronic configurations around neighbouring nuclei in the crystal.

## 7. GENERAL THEORY OF RAMAN SPECTRA.

Classically, elliptically polarised incident light

(7.1) $$\underline{E} = R\left(\underline{A}e^{-i\omega t}\right) = \tfrac{1}{2}\left(\underline{A}e^{-i\omega t} + \underline{A}^* e^{i\omega t}\right)$$

produces an electric moment **M** in the crystal, with rectangular components

(7.2) $$M_\rho = \sum_\sigma \alpha_{\rho\sigma} A_\sigma \qquad (\rho, \sigma = 1,2,3)$$

where $\alpha_{\rho\sigma}$ is the polarisability tensor.

If $\underline{s}$ is a unit vector normal to the direction of observation, then the intensity of the scattered light is

(7.3) $$I = \omega^4 \left|\underline{M}.\underline{s}\right|^2 = \omega^4 \sum_{\rho\sigma}\sum_{\mu\nu} \alpha_{\rho\sigma}\alpha^*_{\mu\nu} A_\sigma A^*_\nu s_\rho s_\mu \ .$$

From the standpoint of quantum mechanics, the intensity of light scattered in a transition from a vibrational state v to another vibrational state v', is then obtained by replacing $\omega^4$ by $(\omega + \omega_{vv'})^4$ and $\alpha_{\rho\sigma}$ by the matrix element $[\alpha_{\rho\sigma}]_{vv'}$; since $\omega_{vv'} \lll \omega$ for all lines excited by a given incident beam, we may put

(7.4) $$\begin{cases} I_{vv'} = \sum_{\rho\sigma}\sum_{\mu\nu} [\alpha_{\rho\sigma}]_{vv'}[\alpha^*_{\mu\nu}]_{vv'} A_\sigma A^*_\nu s_\rho s_\mu \\ \quad\;\; = \sum_{\rho\sigma}\sum_{\mu\nu} [i_{\rho\sigma,\mu\nu}]_{vv'} A_\sigma A^*_\nu s_\rho s_\mu \ . \end{cases}$$

For natural incident light and scattered light observed without an analyser, averages over the polarisation of the incident and scattered light give

(7.5) $$\begin{cases} \overline{A_\rho A^*_\sigma} = -I_0 \cos\theta_\rho \cos\theta_\sigma \ , \quad (\sigma \neq \rho) \ , \\ \overline{A_\rho A^*_\rho} = I_0 \sin^2\theta_\rho \ , \qquad\qquad (\rho,\sigma = 1,2,3) \\ \overline{s_\rho s_\sigma} = -\tfrac{1}{2}\cos\phi_\rho \cos\phi_\sigma \ , \quad (\sigma \neq \rho) \ , \\ \overline{s_\rho s_\rho} = \tfrac{1}{2}\sin^2\phi_\rho \ , \end{cases}$$

where $I_0 = \frac{1}{2}|\underline{A}|^2 = E^2$ = intensity of the incident light, $\theta_\rho$ are the angles between the incident beam and the coordinate axes, and $\phi_\rho$ are the angles between the observed beam and the axes. In particular, if a natural incident beam parallel to a coordinate axis is observed normal to its direction,

$$(7.6) \quad \theta_1 = 0 \; ; \; \theta_2 = \theta_3 = \frac{\pi}{2} \; : \; \phi_1 = \phi_3 = \frac{\pi}{2} \; : \; \phi_2 = 0 ,$$

$$(7.7) \quad \begin{cases} \overline{A_\rho A_\sigma^*} = \overline{s_\rho s_\sigma} = 0 \quad : (\rho \neq \sigma) \\ \overline{A_1 A_1^*} = 0 \; : \; \overline{A_2 A_2^*} = \overline{A_3 A_3^*} = I_0 \\ \overline{s_1 s_1} = \overline{s_3 s_3} = \frac{1}{2} \; : \; \overline{s_2 s_2} = 0 . \end{cases}$$

So

$$(7.8) \quad I_{vv'} = \frac{1}{2} I_0 \left\{ [i_{12,12}]_{vv'} + [i_{23,23}]_{vv'} + [i_{31,31}]_{vv'} + [i_{33,33}]_{vv'} \right\} .$$

Since the last term represents an anisotropic effect depending on the axis normal to the plane of the incident and observed light, we replace it, for cubic crystals, by $\frac{1}{3}\sum_\rho [i_{\rho\rho,\rho\rho}]_{vv'}$.

Hence,

$$(7.9) \quad I_{vv'} = \frac{1}{2} I_0 \left\{ \frac{1}{2} \sum_{\mu,\nu} [i_{\mu\nu,\mu\nu}]_{vv'} + \frac{1}{3} \sum_\mu [i_{\mu\mu,\mu\mu}]_{vv'} \right\} .$$

Considering generally

$$(7.10) \quad [i_{\rho\sigma,\mu\nu}]_{vv'} = [\alpha_{\rho\sigma}]_{vv'} [\alpha^*_{\mu\nu}]_{vv'} ,$$

for all vibrational transitions v to v', since there are many transitions belonging to the same frequency, the weighted mean of this quantity must be calculated.

If $\varepsilon_v$ is the energy of the system in the state v, then

$$(7.11)\qquad \langle i_{e\sigma,\mu\nu}\rangle_{av} = \frac{\sum_v [i_{e\sigma,\mu\nu}]_{vv'}\, e^{-\varepsilon_v/kT}}{\sum_v e^{-\varepsilon_v/kT}},$$

where k = Boltzmann's constant, T is the absolute temperature, and the summation is over the initial state v.

## 8. EXPANSION OF THE POLARISABILITY IN TERMS OF NORMAL COORDINATES.

The equilibrium positions of the nuclei and their small displacements $\underline{u}\binom{l}{k}$ are defined as in Section 1 above. Expanding the polarisability tensor in powers of these displacements,

$$\alpha_{\rho\sigma} = \overset{(0)}{\alpha}_{\rho\sigma} + \overset{(1)}{\alpha}_{\rho\sigma} + \overset{(2)}{\alpha}_{\rho\sigma} + \cdots\cdots, \tag{8.1}$$

where

$$\begin{cases} \overset{(0)}{\alpha}_{\rho\sigma} = \text{constant}, \\ \overset{(1)}{\alpha}_{\rho\sigma} = \sum_{\mu} \sum_{kl} \alpha_{\rho\sigma,\mu}\binom{l}{k} u_{\mu}\binom{l}{k}, \\ \overset{(2)}{\alpha}_{\rho\sigma} = \sum_{\mu\nu} \sum_{kl} \sum_{k'l'} \alpha_{\rho\sigma,\mu\nu}\binom{l\,l'}{k\,k'} u_{\mu}\binom{l}{k} u_{\nu}\binom{l'}{k'}. \end{cases} \tag{8.2}$$

All these quantities are symmetric in $\rho$ and $\sigma$.

The coefficients of the terms in this expansion are derivatives of the polarisability taken in equilibrium and so satisfy certain conditions arising out of the symmetry of the lattice. In addition, the electric moment of the lattice, like the potential energy, is invariant for a rigid translation of the crystal as a whole. Hence

(8.3) $\alpha_{\rho\sigma,\mu}\binom{l}{k}$ is independent of $l$,

$$\alpha_{\rho\sigma,\mu\nu}\binom{l\,l'}{k\,k'} = \alpha_{\rho\sigma,\mu\nu}\binom{l-l'}{k\,k'}, \tag{8.4}$$

$$\sum_{k} \alpha_{\rho\sigma,\mu}(k) = 0, \tag{8.5}$$

$$\sum_{l} \sum_{kk'} \alpha_{\rho\sigma,\mu\nu}\binom{l}{kk'} = 0. \tag{8.6}$$

Following Placzek, we assume that the nuclei form a set of 3sN uncoupled harmonic oscillators. ( N is the number of cells in the crystal.) Then the equations of motion of the nuclei comprise N sets, each of 3s equations of the type

$$\ddot{v}_\alpha\binom{l}{k} + \sum_{l'k'} \sum_{\beta} D_{\alpha\beta}\binom{l-l'}{kk'} v_\beta\binom{l'}{k'} = 0 . \tag{1.9}$$

In Section 1 these equations were solved by introducing a plane wave, but here we introduce complex normal coordinates $\xi\binom{q}{j}$. Then

$$\underline{v}\binom{l}{k} = \sqrt{m_k}\,\underline{u}\binom{l}{k} = \sum_{qj} \underline{e}\left(k\middle|\begin{smallmatrix}q\\ j\end{smallmatrix}\right) e^{i(q\cdot \underline{r}^l)}\, \xi\binom{q}{j}, \tag{8.7}$$

and (1.9) becomes

$$\omega^2\binom{q}{j} e_\alpha\left(k\middle|\begin{smallmatrix}q\\ j\end{smallmatrix}\right) - \sum_{k'} \sum_{\beta} D_{\alpha\beta}\binom{q}{kk'} e_\beta\left(k'\middle|\begin{smallmatrix}q\\ j\end{smallmatrix}\right) = 0 \tag{8.8}$$

where $j = 1,2,3,\ldots,3s$. (Cf. (1.11).) The choice of possible wave-vectors $\underline{q}$ is restricted as before by the condition of the cyclic lattice.

The $e_\alpha\left(k\middle|\begin{smallmatrix}q\\ j\end{smallmatrix}\right)$ are the components of the eigen-vectors of the lattice corresponding to the frequency $\omega\binom{q}{j}$ and satisfy the orthogonality relations

$$\left\{\begin{aligned} &\sum_{\alpha,k} e_\alpha\left(k\middle|\begin{smallmatrix}q\\ j\end{smallmatrix}\right) e^*_\alpha\left(k\middle|\begin{smallmatrix}q\\ j'\end{smallmatrix}\right) = \delta(jj'), \\ &\sum_{j} e_\alpha\left(k\middle|\begin{smallmatrix}q\\ j\end{smallmatrix}\right) e^*_\beta\left(k'\middle|\begin{smallmatrix}q\\ j\end{smallmatrix}\right) = \delta(\alpha\beta).\,\delta(kk'). \end{aligned}\right. \tag{8.9}$$

Each complex $\xi\binom{q}{j}$ represents two real normal coordinates, but since

$$\xi\binom{-q}{j} = \xi^*\binom{q}{j} , \tag{8.10}$$

restriction of the values of q to half the unit cell of reciprocal space reduces the number of coordinates to the correct value.

Substituting (8.7) in (8.2)

$$(8.11) \quad \overset{(1)}{\alpha}_{\varrho\sigma} = \sum_{qj}\sum_{\mu}\sum_{lk} \frac{1}{\sqrt{m_k}} \alpha_{\varrho\sigma,\mu}(k)\, e^{i(q\cdot r^l)}\, e_\mu(k|{}^q_j)\, \xi({}^q_j).$$

The factor $\sum_l' e^{i(q\cdot r^l)}$ is a $\delta$-function of q and is zero unless $q = 0$. Hence

$$(8.12) \quad \overset{(1)}{\alpha}_{\varrho\sigma} = \sum_j \alpha_{\varrho\sigma}({}^0_j)\, \xi({}^0_j),$$

where

$$(8.13) \quad \alpha_{\varrho\sigma}({}^0_j) = \sum_k \sum_\mu \alpha_{\varrho\sigma,\mu}(k)\, e_\mu(k|{}^0_j) \frac{1}{\sqrt{m_k}}.$$

The matrix elements $[\xi({}^0_j)]_{vv'}$ vanish except for transitions v to v' belonging to the frequencies $\pm\omega({}^0_j)$ ; so the first-order Raman effect is a spectrum of $3s-3$ lines. (The 3 acoustic branches of the frequency spectrum of a crystal have $\omega({}^0_j)=0$.) This line spectrum does not exist if each lattice point of the crystal is a centre of symmetry, for in that case $\overset{(1)}{\alpha}_{\varrho\sigma} = 0$.

The second-order polarisability becomes

$$(8.14) \quad \overset{(2)}{\alpha}_{\varrho\sigma} = \sum_{qj}\sum_{q'j'}\sum_{\mu\nu}\sum_{lk}\sum_{l'k'} \alpha_{\varrho\sigma,\mu\nu}\left({}^{l-l'}_{kk'}\right) e^{i(q\cdot r^l + q'\cdot r^{l'})} \cdot e_\mu(k|{}^q_j)\, e_\nu(k'|{}^{q'}_{j'}) \frac{\xi({}^q_j)\xi({}^{q'}_{j'})}{\sqrt{m_k m_{k'}}}$$

Substituting $l$ for $(l-l')$, the factor $\sum_{l'} e^{i(r^{l'}\cdot \overline{q+q'})}$ is a $\delta$-function of $\overline{q+q'}$. So using (8.10)

$$(8.15) \quad \overset{(2)}{\alpha}_{\varrho\sigma} = \sum_q \sum_{jj'} \alpha_{\varrho\sigma}\left({}^{q}_{jj'}\right) \xi({}^q_j)\, \xi^*({}^q_{j'}),$$

where

$$(8.16)\quad \alpha_{\varrho\sigma}\left(\begin{smallmatrix} q \\ jj' \end{smallmatrix}\right) = \sum_{\ell} \sum_{kk'} \sum_{\mu\nu} \alpha_{\varrho\sigma,\mu\nu}\left(\begin{smallmatrix} \ell \\ kk' \end{smallmatrix}\right) e^{i(q.r^{\ell})} \cdot e_{\mu}\left(k\middle|\begin{smallmatrix} q \\ j \end{smallmatrix}\right) e_{\nu}^{*}\left(k'\middle|\begin{smallmatrix} q \\ j' \end{smallmatrix}\right) \frac{1}{\sqrt{m_k m_{k'}}}.$$

## 9. CALCULATION OF THE INTENSITY DISTRIBUTION.

Consider first a set of real oscillators characterised by quantum numbers $v_j$. The matrix elements $[\eta_j]_{vv'}$ of the amplitude of one of these oscillators are zero unless $v_j$ changes by $\pm 1$ while all the other $v_{j'}$ are unchanged. The matrix elements $[\eta_j^2]_{vv'}$ of the square of the amplitude are zero unless $v_j$ changes by 0 or $\pm$ 2, and the matrix elements $[\eta_j \eta_{j'}]_{vv'}$ $(j \neq j')$ of the product are zero unless $v_j$ and $v_{j'}$ both change by $\pm 1$.

The non-vanishing elements can be arranged according to the frequencies

(9.1) $$\omega_{vv'} = \sum_j \omega_j (v_j - v_j'),$$

and are set out below in Table 10, where $c_j = \sqrt{\frac{\hbar}{2\omega_j}}$.

Table 10.

| | $\eta_j$ | $\eta_j \eta_{j'}$ | $\eta_j^2$ |
|---|---|---|---|
| $0$ | | | $c_j^2(2v_j + 1)$ |
| $+\omega_j$ | $c_j\sqrt{v_j+1}$ | | |
| $-\omega_j$ | $c_j\sqrt{v_j}$ | | |
| $+2\omega_j$ | | | $c_j^2\sqrt{(v_j+1)(v_j+2)}$ |
| $-2\omega_j$ | | | $c_j^2\sqrt{v_j(v_j-1)}$ |
| $\omega_j+\omega_{j'}$ | | $c_j c_{j'}\sqrt{(v_j+1)(v_{j'}+1)}$ | |
| $-(\omega_j+\omega_{j'})$ | | $c_j c_{j'}\sqrt{v_j v_{j'}}$ | |
| $\omega_j - \omega_{j'}$ | | $c_j c_{j'}\sqrt{v_{j'}(v_j+1)}$ | |

Further, a product of the form

(9.2) $$\langle [\eta_j]_{vv'} [\eta_{j'}]_{vv'} \rangle_{av.}$$

will be zero unless both factors refer to the same oscillator, and a product

(9.3) $$\langle [\eta_j \eta_{j'}]_{vv'} [\eta_{j''} \eta_{j'''}]_{vv'} \rangle_{av}$$

will be zero unless the first factor refers to the same pair of oscillators as the second, i.e. unless $j = j''$, $j' = j'''$, or $j = j'''$, $j' = j''$.

For complex oscillators $\xi_j = \eta_j + i\zeta_j$ , the thermal average of the amplitude product

(9.4) $$\langle [\xi_j]_{vv'} [\xi_j^*]_{vv'} \rangle_{av} = 2 \langle [\eta_j]^2_{vv'} \rangle_{av} .$$

Omitting the case $v = v'$ (Rayleigh scattering), there are three possible ways of choosing the indices j in the second-order amplitude products. The thermal averages corresponding to these three ways are:

(1): $j = j' = j'' = j'''$:

(9.5) $$\langle [\xi_j \xi_j^*]^2_{vv'} \rangle_{av} = 2 \langle [\eta_j^2]^2_{vv'} \rangle_{av} :$$

(2) : $j = j''$: $j' = j'''$: $j \neq j'$:

(9.6) $$\langle [\xi_j \xi_{j'}^*]_{vv'} [\xi_j^* \xi_{j'}]_{vv'} \rangle_{av} = 4 \langle [\eta_j \eta_{j'}]^2_{vv'} \rangle_{av} :$$

(3): $j = j'''$: $j' = j''$ : $j \neq j'$ :

(9.7) $$\langle [\xi_j \xi_{j'}^*]_{vv'} [\xi_j \xi_{j'}^*]_{vv'} \rangle_{av} = 0 .$$

The thermal averages for the real oscillators are obtained from (7.11) and Table 10, and are given in Table 11 below.

Table 11.

| | $\langle[\eta_j]^2_{vv'}\rangle_{av}$ | $\langle[\eta_j^2]^2_{vv'}\rangle_{av.}$ | $\langle[\eta_j\,\eta_{j'}]^2_{vv'}\rangle_{av}$ |
|---|---|---|---|
| $+\omega_j$ | $C(j)e^{-\beta_j}$ | | |
| $-\omega_j$ | $C(j)$ | | |
| $+2\omega_j$ | | $2C(j)^2e^{-2\beta_j}$ | |
| $-2\omega_j$ | | $2C(j)^2$ | |
| $\omega_j+\omega_{j'}$ | | | $C(j)C(j')e^{-\beta_j-\beta_{j'}}$ |
| $-(\omega_j+\omega_{j'})$ | | | $C(j)C(j')$ |
| $\omega_j-\omega_{j'}$ | | | $C(j)C(j')e^{-\beta_j}$ |

The abbreviations used are

$$(9.8)\qquad \beta_j = \frac{\hbar\omega_j}{kT} \quad ; \quad C(j) = \frac{c_j^2}{1-e^{-\beta_j}} \quad .$$

Hence for the first-order effect, from (7.10), (8.12), (9.4) and Table 11, the intensity of a single transition is

$$(9.9)\quad i_{\varrho\sigma,\mu\nu}\binom{0}{j} = 2C(j)\left\{\alpha_{\varrho\sigma}\binom{0}{j}\alpha^*_{\mu\nu}\binom{0}{j}\right\}\begin{cases} 1 & \text{(Stokes line)} \\ e^{-\beta_j} & \text{(Anti-Stokes line).}\end{cases}$$

The Stokes lines are the frequency shifts $-\omega\binom{0}{j}$ and the anti-Stokes lines the frequency shifts $+\omega\binom{0}{j}$.

Similarly from (7.10), (8.15), (9.5), (9.6), and Table 11, the intensity of a single second-order transition is

$$(9.10)\quad i_{e\sigma,\mu\nu}\binom{q}{jj'} = 2C\binom{q}{j}C\binom{q}{j'}\left\{\alpha_{e\sigma}\binom{q}{jj'}\alpha^*_{\mu\nu}\binom{q}{jj'} + \alpha_{e\sigma}\binom{q}{j'j}\alpha^*_{\mu\nu}\binom{q}{j'j}\right\}\cdot$$

$$\cdot\begin{cases} \text{Stokes} & \text{A-Stokes} \\ 1 & e^{-\beta\binom{q}{j}-\beta\binom{q}{j'}} \\ e^{-\beta\binom{q}{j'}} & e^{-\beta\binom{q}{j}} \end{cases},$$

corresponding to the frequencies

$$(9.11)\qquad \omega\binom{q}{jj'} = \begin{cases} \omega\binom{q}{j} + \omega\binom{q}{j'} \\ \omega\binom{q}{j} - \omega\binom{q}{j'} \end{cases}.$$

Then the intensity of a first-order line excited by an incident beam $\underline{A}$ and scattered in a direction $\underline{s}$ is, from (7.4),

$$(9.12)\quad I(j) = \sum_{e\sigma,\mu\nu} i_{e\sigma,\mu\nu}\binom{0}{j}\overline{A_e A^*_\mu}\,\overline{S_\sigma S_\nu} \qquad (j = 1,2,3,..(3s-3))$$

To calculate the observed second-order intensity, the single transition intensity (9.10) has to be integrated over the part of reciprocal space $0 \leq \underline{q} \leq 1$ which belongs to the appropriate frequency $\omega\binom{q}{jj'}$:

$$(9.13)\quad i_{e\sigma,\mu\nu}(\omega)\,d\omega = \sum_{jj'} \iiint\limits_{\omega < \left|\omega\binom{q}{jj'}\right| < \omega + d\omega} i_{e\sigma,\mu\nu}\binom{q}{jj'}\,dq_1\,dq_2\,dq_3 .$$

Then the total second-order intensity produced by incident light $\underline{A}$ scattered in the direction $\underline{s}$, is

$$(9.14)\quad I(\omega) = \sum_{e\sigma,\mu\nu} i_{e\sigma,\mu\nu}(\omega)\,\overline{A_e A^*_\mu}\,\overline{S_\sigma S_\nu} .$$

If the lattice has more than one particle in the unit cell, then the optical branches of the frequency spectrum tend to finite limits as $\underline{q}$ approaches zero. Consequently the range of integration in (9.13) has to be split into two parts, one part containing the single point $\underline{q} = 0$, and the other, the rest of the allowed range. At the point $\underline{q} = 0$ the summed integral (9.13) reduces to a sum over j and j' in which there are $(3s)^2$ terms. The frequency shifts corresponding to these terms are sums and differences of the (3s-3) first-order Raman frequencies, so there will be $3s(3s-3)$ second-order lines ( $3(3s-3)$ of these will coincide with the first-order lines); 9 terms belong to combinations of the acoustic branches and have zero frequency shift.

The summed integral (9.13) taken over the remainder of the allowed part of reciprocal space has $(3s)^2$ terms. Hence the observed spectrum will also contain $(3s)^2$ continuous bands, each one of which has a maximum at a certain point. The result of the superposition of these bands is a continuous background with a large number of peaks.

## 10. CALCULATION OF THE RAMAN SPECTRUM OF DIAMOND.

(a). First-order line spectrum.

The polarisability terms occurring in (9.9) are given explicitly by (8.13):

(8.13) $$\alpha_{\varrho\sigma}\binom{0}{j} = \sum_{k}\sum_{\mu}\frac{1}{\sqrt{m_k}}\alpha_{\varrho\sigma,\mu}(k).e_\mu\left(k\middle|\begin{matrix}0\\j\end{matrix}\right),$$

where for diamond, $k = 1$ or $2$, $j = 1,2,3,4,5,6,$ and $m_1 = m_2 = m$.

From the invariance condition (8.5),

(10.1) $$\alpha_{\varrho\sigma,\mu}(1) + \alpha_{\varrho\sigma,\mu}(2) = 0,$$

and by applying the matrices of the symmetry operations given in Section 2 above, we find

(10.2) $$\begin{cases} \alpha_{12,3}(1) = \alpha_{23,1}(1) = \alpha_{31,2}(1) \\ \qquad = -\alpha_{12,3}(2) = -\alpha_{23,1}(2) = -\alpha_{31,2}(2) = n. \end{cases}$$

The remaining $\alpha_{\varrho\sigma,\mu}(k)$ are all zero.

The eigen-vectors $e_\mu(k|j)$ at the point $\underline{q} = 0$ are the normalised latent vectors of the dynamical matrix $D(q)$ at $\underline{q} = 0$, viz.

(10.3) $$\begin{cases}
e_1(1|1) = 1/\sqrt{2}: & e_2(1|1) = 0 : & e_3(1|1) = 0 : \\
e_1(1|2) = 0 : & e_2(1|2) = 1/\sqrt{2}: & e_3(1|2) = 0 : \\
e_1(1|3) = 0 : & e_2(1|3) = 0 : & e_3(1|3) = 1/\sqrt{2}: \\
e_1(1|4) = 1/\sqrt{2}: & e_2(1|4) = 0 : & e_3(1|4) = 0 : \\
e_1(1|5) = 0 : & e_2(1|5) = 1/\sqrt{2}: & e_3(1|5) = 0 : \\
e_1(1|6) = 0 ; & e_2(1|6) = 0 : & e_3(1|6) = 1/\sqrt{2}: \\
e_1(2|1) = -1/\sqrt{2}: & e_2(2|1) = 0 : & e_3(2|1) = 0 : \\
e_1(2|2) = 0 : & e_2(2|2) = -1/\sqrt{2}: & e_3(2|2) = 0 : \\
e_1(2|3) = 0 : & e_2(2|3) = 0 : & e_3(2|3) = -1/\ 2: \\
e_1(2|4) = 1/\sqrt{2}: & e_2(2|4) = 0 : & e_3(2|4) = 0 : \\
e_1(2|5) = 0 : & e_2(2|5) = 1/\sqrt{2}: & e_3(2|5) = 0 : \\
e_1(2|6) = 0 : & e_2(2|6) = 0 : & e_3(2|6) = 1/\sqrt{2}:
\end{cases}$$

corresponding to the frequencies

$$(3.19) \quad \begin{cases} \omega(1) = \omega(2) = \omega(3) = \sqrt{\frac{8\alpha}{m}}, \\ \omega(4) = \omega(5) = \omega(6) = 0. \end{cases}$$

Substituting in (8.13),

$$(10.4) \quad \alpha_{11}\binom{0}{j} = \alpha_{22}\binom{0}{j} = \alpha_{33}\binom{0}{j} = 0, \quad \text{for all } j,$$

$$(10.5) \quad \alpha_{12}\binom{0}{j} = 0, \qquad \text{for } j = 1,2,4,5,6,$$

$$(10.6) \quad \alpha_{23}\binom{0}{j} = 0, \qquad \text{for } j = 2,3,4,5,6,$$

$$(10.7) \quad \alpha_{31}\binom{0}{j} = 0, \qquad \text{for } j = 1,3,4,5,6,$$

$$(10.8) \quad \alpha_{12}\binom{0}{3} = \alpha_{23}\binom{0}{1} = \alpha_{31}\binom{0}{2} = \sqrt{\frac{2}{m}}\cdot n.$$

But for a natural incident beam observed normal to its direction without an analyser,

$$(7.9) \quad I_{vv'} = \tfrac{1}{2} I_0 \left\{ \tfrac{1}{2} \sum_{\mu,\nu} [i_{\mu\nu,\mu\nu}]_{vv'} + \tfrac{1}{3} \sum_{\mu} [i_{\mu\mu,\mu\mu}]_{vv'} \right\},$$

so we have to form the quantities A(j) given by

$$(10.9) \quad A(j) = \tfrac{1}{2} \sum_{\mu,\nu} \left| \alpha_{\mu\nu}\binom{0}{j} \right|^2 + \tfrac{1}{3} \sum_{\mu} \left| \alpha_{\mu\mu}\binom{0}{j} \right|^2.$$

From (10.4) - (10.8),

$$(10.10) \quad \begin{cases} A(1) = A(2) = A(3) = 2n^2/m, \\ A(4) = A(5) = A(6) = 0. \end{cases}$$

Since $\omega(1) = \omega(2) = \omega(3)$,

$$(10.11) \quad \beta(1) = \beta(2) = \beta(3) \; : \; C(1) = C(2) = C(3),$$

so the intensity of the single first-order line is

$$(10.12) \quad I(j) = 3 I_0 . A(1) . C(1) \begin{cases} 1 & \text{(Stokes line)} \\ \text{or} & \\ e^{-\beta(1)} & \text{(Anti-Stokes line)} \end{cases}.$$

(b). Second-order spectrum.

The polarisability terms in (9.10) are given by (8.16):

$$(8.16)\quad \alpha_{\rho\sigma}\begin{pmatrix} q \\ j\,j' \end{pmatrix} = \sum_{l} \sum_{kk'} \sum_{\mu\nu} \alpha_{\rho\sigma,\mu\nu}\begin{pmatrix} l \\ kk' \end{pmatrix} e^{i(\underline{q}\cdot\underline{r}^{l})} \cdot e_{\mu}\left(k \middle| \begin{matrix} q \\ j \end{matrix}\right) e_{\nu}^{*}\left(k' \middle| \begin{matrix} q \\ j' \end{matrix}\right) \cdot \frac{1}{\sqrt{m_k m_{k'}}},$$

where k,k' = 1 or 2, j,j' = 1,2,3,4,5,6, and $m_1 = m_2 = m$.

First consider the constants $\alpha_{\rho\sigma,\mu\nu}\begin{pmatrix} l \\ kk' \end{pmatrix}$: the $\begin{pmatrix} l \\ kk' \end{pmatrix}$ label the bonds between a nucleus $\begin{pmatrix} 0 \\ k' \end{pmatrix}$ of the base cell and some other nucleus $\begin{pmatrix} l \\ k \end{pmatrix}$. The number of independent $\alpha_{\rho\sigma,\mu\nu}\begin{pmatrix} l \\ kk' \end{pmatrix}$ can be reduced by applying the symmetry operations of the lattice and the invariance condition (8.6). In the diamond lattice, each nucleus in the unit cell has four first neighbours and twelve second neighbours; to account for the observed specific heat it is necessary to assume central forces between second neighbours. If the polarisability were taken to the same approximation as the dynamical matrix $D\begin{pmatrix} l \\ kk' \end{pmatrix}$, there would be in all 32 different values of $\begin{pmatrix} l \\ kk' \end{pmatrix}$ to consider. But these $\alpha_{\rho\sigma,\mu\nu}\begin{pmatrix} l \\ kk' \end{pmatrix}$ are derivatives of the polarisability of the crystal taken in equilibrium and so depend on the interaction between the electrons surrounding neighbouring nuclei in the lattice. The determination of this interaction is a perturbation problem in quantum mechanics which will not be considered here. Therefore, to reduce the number of arbitrary constants appearing in the intensity factors to a minimum, we shall assume that the $\alpha_{\rho\sigma,\mu\nu}\begin{pmatrix} l \\ kk' \end{pmatrix}$ are zero for all neighbours except the first.

Labelling the bonds $\binom{l}{kk'}$ as in Table 1, Section 2, the 10 independent $\alpha_{\rho\sigma,\mu\nu}\binom{l}{kk'}$ are;

$$(10.13)\qquad \begin{cases} \alpha_{11,11}(1) = a, \\ \alpha_{11,22}(1) = \alpha_{11,33}(1) = b, \\ \alpha_{11,12}(1) = c, \\ \alpha_{11,23}(1) = d, \\ \alpha_{11,31}(1) = e, \\ \alpha_{12,11}(1) = \alpha_{12,22}(1) = f, \\ \alpha_{12,33}(1) = g, \\ \alpha_{12,12}(1) = h, \\ \alpha_{12,23}(1) = j, \\ \alpha_{12,31}(1) = k. \end{cases}$$

All the other non-zero $\alpha_{\rho\sigma,\mu\nu}\binom{l}{kk'}$ can be obtained from these by the use of the symmetry operations of Section 2 and the invariance condition (8.6).

Now consider the eigen-vectors $e_\mu(k|{}^{q}_{j})$. There is no difficulty about the second-order line spectrum, for the range of integration in (9.13) is the single point $\underline{q} = 0$, and the eigen-vectors required are given in (10.3) above. But for the continuous part of the spectrum, although the eigen-vectors could be found for each point of reciprocal space for which the corresponding frequencies $\omega\binom{q}{j}$ are already known, the calculations would be lengthy and tedious. The frequencies $\omega\binom{q}{jj'}$ as functions of q, are stationary at the point $\underline{q} = (\frac{1}{2},\frac{1}{2},\frac{1}{2})$ (cf. fig. 4 above); the frequency density $z_{jj'}(\omega)$ of $\omega\left({q \atop jj'}\right)$, given by

$$(10.14) \qquad z_{jj'}(\omega)\,d\omega = \iiint\limits_{\omega < \left|\omega\left({q \atop jj'}\right)\right| < \omega + d\omega} dq_1\,dq_2\,dq_3\,,$$

will be a maximum at this point. Thus a first approximation to the summed integral (9.13) is

$$(10.15) \qquad i_{e\sigma,\mu\nu}(\omega) = \sum_{jj'} i_{e\sigma,\mu\nu}\left({q \atop jj'}\right) z_{jj'}(\omega)$$

where $\underline{q} = (\frac{1}{2},\frac{1}{2},\frac{1}{2})$.

At the point $\underline{q} = 0$, (8.16) becomes

$$(10.16) \quad \begin{aligned}
\alpha_{11}\left({0 \atop jj'}\right) = \frac{4a}{m} &\left\{ \begin{aligned} &-e_1(1|{0 \atop j})\,e_1^*(1|{0 \atop j'}) - e_1(2|{0 \atop j})\,e_1^*(2|{0 \atop j'}) \\ &\qquad + e_1(1|{0 \atop j})\,e_1^*(2|{0 \atop j'}) + e_1(2|{0 \atop j})\,e_1^*(1|{0 \atop j'}) \end{aligned} \right\} \\
+ \frac{4b}{m} &\left\{ \begin{aligned} &-e_2(1|{0 \atop j})\,e_2^*(1|{0 \atop j'}) - e_2(2|{0 \atop j})\,e_2^*(2|{0 \atop j'}) \\ &\qquad + e_2(1|{0 \atop j})\,e_2^*(2|{0 \atop j'}) + e_2(2|{0 \atop j})\,e_2^*(1|{0 \atop j'}) \\ &-e_3(1|{0 \atop j})\,e_3^*(1|{0 \atop j'}) - e_3(2|{0 \atop j})\,e_3^*(2|{0 \atop j'}) \\ &\qquad + e_3(1|{0 \atop j})\,e_3^*(2|{0 \atop j'}) + e_3(2|{0 \atop j})\,e_3^*(1|{0 \atop j'}) \end{aligned} \right\}, \\
\alpha_{12}\left({0 \atop jj'}\right) = \frac{4h}{m} &\left\{ \begin{aligned} &-e_1(1|{0 \atop j})\,e_2^*(1|{0 \atop j'}) - e_2(1|{0 \atop j})\,e_1^*(1|{0 \atop j'}) \\ &\qquad - e_1(2|{0 \atop j})\,e_2^*(2|{0 \atop j'}) - e_2(2|{0 \atop j})\,e_1^*(2|{0 \atop j'}) \\ &+e_1(1|{0 \atop j})\,e_2^*(2|{0 \atop j'}) + e_2(1|{0 \atop j})\,e_1^*(2|{0 \atop j'}) \\ &\qquad + e_1(2|{0 \atop j})\,e_2^*(1|{0 \atop j'}) + e_2(2|{0 \atop j})\,e_1^*(1|{0 \atop j'}) \end{aligned} \right\}.
\end{aligned}$$

Substituting the eigen-vectors (10.3),

$$(10.17) \quad \left\{ \begin{aligned}
&\alpha_{11}\left({0 \atop 11}\right) = -\frac{8a}{m} : \alpha_{11}\left({0 \atop 22}\right) = -\frac{8b}{m} : \alpha_{11}\left({0 \atop 33}\right) = -\frac{8b}{m} : \\
&\alpha_{22}\left({0 \atop 11}\right) = -\frac{8b}{m} : \alpha_{22}\left({0 \atop 22}\right) = -\frac{8a}{m} : \alpha_{22}\left({0 \atop 33}\right) = -\frac{8b}{m} : \\
&\alpha_{33}\left({0 \atop 11}\right) = -\frac{8b}{m} : \alpha_{33}\left({0 \atop 22}\right) = -\frac{8b}{m} : \alpha_{33}\left({0 \atop 33}\right) = -\frac{8a}{m} : \\
&\alpha_{12}\left({0 \atop 12}\right) = \alpha_{23}\left({0 \atop 23}\right) = \alpha_{13}\left({0 \atop 13}\right) = -\frac{8h}{m}\,.
\end{aligned} \right.$$

All other $\alpha_{\rho\sigma}\binom{0}{jj'}$ are zero.

Now let

(10.18) $A\binom{0}{jj'} = \frac{1}{2}\sum_{\mu,\nu}\left|\alpha_{\mu\nu}\binom{0}{jj'}\right|^2 + \frac{1}{3}\sum_{\mu}\left|\alpha_{\mu\mu}\binom{0}{jj'}\right|^2;$

so

(10.19) $\begin{cases} A\binom{0}{11} = A\binom{0}{22} = A\binom{0}{33} = \frac{64}{3m^2}(a^2+2b^2), \\ A\binom{0}{12} = A\binom{0}{23} = A\binom{0}{13} = \frac{64}{m^2}\cdot h^2. \end{cases}$

Since $\omega\binom{0}{j} = \omega\binom{0}{j'}$ for j,j' = 1,2,3,

(10.20) $\omega\binom{0}{jj'} = \omega\binom{0}{j} + \omega\binom{0}{j'} = 2\omega\binom{0}{j} = 2\sqrt{\frac{8\alpha}{m}},$

and

(10.21) $\omega\binom{0}{jj'} = \omega\binom{0}{j} - \omega\binom{0}{j'} = 0.$

Hence $C\binom{0}{j} = C\binom{0}{j'}$ and $\beta\binom{0}{j} = \beta\binom{0}{j'}$ for j,j' = 1,2,3, and there will be a single second-order Raman line for diamond with a frequency shift $\omega\binom{0}{jj'} = 2\sqrt{\frac{8\alpha}{m}}$ and intensity, from (7.9) and (9.10),

(10.22) $I\binom{0}{jj'} = \frac{1}{2}I_0\sum_{jj'}A\binom{0}{jj'}\,2C\binom{0}{j}^2\begin{cases} 1 & \text{(Stokes line)} \\ \text{or} & \\ e^{-2\beta\binom{0}{j}} & \text{(A. Stokes line).} \end{cases}$

At the point $\underline{q} = (\frac{1}{2},\frac{1}{2},\frac{1}{2})$, (8.16) becomes

$$
\begin{aligned}
\alpha_{11}\binom{q}{jj'} = & -\frac{2a}{m}\Big\{ 2e_1(1|j)\,e_1^*(1|j') + 2e_1(2|j)\,e_1^*(2|j') \\
& \qquad + e_1(1|j)\,e_1^*(2|j') + e_1(2|j)\,e_1^*(1|j') \Big\} \\
& -\frac{2b}{m}\Big\{ 2e_2(1|j)\,e_2^*(1|j') + 2e_2(2|j)\,e_2^*(2|j') \\
& \qquad + e_2(1|j)\,e_2^*(2|j') + e_2(2|j)\,e_2^*(1|j') \\
& \qquad + 2e_3(1|j)\,e_3^*(1|j') + 2e_3(2|j)\,e_3^*(2|j') \\
& \qquad + e_3(1|j)\,e_3^*(2|j') + e_3(2|j)\,e_3^*(1|j') \Big\} \\
& +\frac{2c}{m}\Big\{ e_1(1|j)\,e_2^*(2|j') + e_1(1|j)\,e_3^*(2|j') \\
& \qquad + e_1(2|j)\,e_2^*(1|j') + e_1(2|j)\,e_3^*(1|j') \Big\} \\
& +\frac{2d}{m}\Big\{ e_2(1|j)\,e_3^*(2|j') + e_3(1|j)\,e_2^*(2|j') \\
& \qquad + e_2(2|j)\,e_3^*(1|j') + e_3(2|j)\,e_2^*(1|j') \Big\} \\
& +\frac{2e}{m}\Big\{ e_3(1|j)\,e_1^*(2|j') + e_2(1|j)\,e_1^*(2|j') \\
& \qquad + e_3(2|j)\,e_1^*(1|j') + e_2(2|j)\,e_1^*(1|j') \Big\},
\end{aligned}
\tag{10.23}
$$

$$
\begin{aligned}
\alpha_{12}\binom{q}{jj'} = & +\frac{2f}{m}\Big\{ e_1(1|j)\,e_1^*(2|j') + e_2(1|j)\,e_2^*(2|j') \\
& \qquad + e_1(2|j)\,e_1^*(1|j') + e_2(2|j)\,e_2^*(1|j') \Big\} \\
& +\frac{2g}{m}\Big\{ e_3(1|j)\,e_3^*(2|j') + e_3(2|j)\,e_3^*(1|j') \Big\} \\
& -\frac{2h}{m}\Big\{ 2e_1(1|j)\,e_2^*(1|j') + 2e_2(1|j)\,e_1^*(1|j') \\
& \qquad + 2e_1(2|j)\,e_2^*(2|j') + 2e_2(2|j)\,e_1^*(2|j') \\
& \qquad + e_1(1|j)\,e_2^*(2|j') + e_2(1|j)\,e_1^*(2|j') \\
& \qquad + e_1(2|j)\,e_2^*(1|j') + e_2(2|j)\,e_1^*(1|j') \Big\} \\
& +\frac{2j}{m}\Big\{ e_1(1|j)\,e_3^*(2|j') + e_2(1|j)\,e_3^*(2|j') \\
& \qquad + e_1(2|j)\,e_3^*(1|j') + e_2(2|j)\,e_3^*(1|j') \Big\} \\
& +\frac{2k}{m}\Big\{ e_3(1|j)\,e_1^*(2|j') + e_3(1|j)\,e_2^*(2|j') \\
& \qquad + e_3(2|j)\,e_1^*(1|j') + e_3(2|j)\,e_2^*(1|j') \Big\}.
\end{aligned}
\tag{10.24}
$$

The eigen-vectors $\underline{e}(k|{}^{q}_{j})$ at $\underline{q} = (\frac{1}{2},\frac{1}{2},\frac{1}{2})$ are the normalised latent vectors of the dynamical matrix $D(q)$ at that point. From (3.6) and (3.18) they are as follows:-

$$
(10.25)\quad \left\{\begin{array}{llll}
e_1(1|1) = 1/2 & : e_2(1|1) = -1/2 & : e_3(1|1) = 0 & : \\
e_1(1|2) = 1/2\sqrt{3} & : e_2(1|2) = 1/2\sqrt{3} & : e_3(1|2) = -1/\sqrt{3} & : \\
e_1(1|3) = 1/\sqrt{6} & : e_2(1|3) = 1/\sqrt{6} & : e_3(1|3) = 1/\sqrt{6} & : \\
e_1(1|4) = 1/\sqrt{6} & : e_2(1|4) = 1/\sqrt{6} & : e_3(1|4) = 1/\sqrt{6} & : \\
e_1(1|5) = 1/2 & : e_2(1|5) = -1/2 & : e_3(1|5) = 0 & : \\
e_1(1|6) = 1/2\sqrt{3} & : e_2(1|6) = 1/2\sqrt{3} & : e_3(1|6) = -1/\sqrt{3} & : \\
e_1(2|1) = 1/2 & : e_2(2|1) = -1/2 & : e_3(2|1) = 0 & : \\
e_1(2|2) = 1/2\sqrt{3} & : e_2(2|2) = 1/2\sqrt{3} & : e_3(2|2) = -1/\sqrt{3} & : \\
e_1(2|3) = 1/\sqrt{6} & : e_2(2|3) = 1/\sqrt{6} & : e_3(2|3) = 1/\sqrt{6} & : \\
e_1(2|4) = -1/\sqrt{6} & : e_2(2|4) = -1/\sqrt{6} & : e_3(2|4) = -1/\sqrt{6} & : \\
e_1(2|5) = -1/2 & : e_2(2|5) = 1/2 & : e_3(2|5) = 0 & : \\
e_1(2|6) = -1/2\sqrt{3} & : e_2(2|6) = -1/2\sqrt{3} & : e_3(2|6) = 1/\sqrt{3}. &
\end{array}\right.
$$

These values are inserted in (10.23) and (10.24) and a lengthy calculation leads to the following values of

$$A(jj') = \frac{1}{2}\sum_{\mu,\nu}\left|\alpha_{\mu\nu}\binom{q}{jj'}\right|^2 + \frac{1}{3}\sum_{\mu}{}'\left|\alpha_{\mu\mu}\binom{q}{jj'}\right|^2$$

at the point $\underline{q} = (\frac{1}{2},\frac{1}{2},\frac{1}{2})$:

$$m^2 A(11) = \frac{1}{3}\left[2(3a+3b+c+e)^2 + 4(3b+d)^2\right] + 2(f+g-j-k)^2 + 4(f+3h)^2,$$

$$m^2 A(22) = \frac{1}{27}\left[2(3a+15b+c+4d+e)^2 + 4(6a+3b+2c-d+2e)^2\right] + \frac{2}{9}(5f+g+12h-j-k)^2 + \frac{4}{9}(f+2g-3h-2j-2k)^2,$$

$$m^2A(33) = \frac{4}{9}(3a+6b-2c-2d-2e)^2$$
$$+ \frac{4}{3}(2f+g-6h+2j+2k)^2,$$

$$m^2A(44) = \frac{4}{9}(a+2b+2c+2d+2e)^2$$
$$+ \frac{4}{3}(2f+g+2h+2j+2k)^2,$$

$$m^2A(55) = \frac{1}{3}\left[2(a+b-c-e)^2 + 4(b-d)^2\right.$$
$$\left.+2(f+g-j-k)^2 + 4(f-h)^2\right],$$

$$m^2A(66) = \frac{1}{27}\left[2(a+5b-c-4d-e)^2 + 4(2a+b-2c+d-2e)^2\right]$$
$$+\frac{2}{9}(5f+g-4h-j-k)^2 + \frac{4}{9}(f+2g+h-2j-2k)^2,$$

$$m^2A(12) = \frac{2}{9}(3a-3b+c-2d+e)^2$$
$$+ \frac{2}{3}(f-g+6h+j+k)^2,$$

$$m^2A(13) = m^2A(23)$$
$$= \frac{4}{9}(3a-3b-2c+d+e)^2$$
$$+ \frac{4}{3}(f-g-3h+j-2k)^2,$$

$$m^2A(45) = m^2A(46)$$
$$= \frac{4}{9}(a-b-c-d+2e)^2$$
$$+\frac{4}{3}(f-g+h-2j+k)^2,$$

$$m^2A(56) = \frac{2}{9}(a-b-c+2d-e)^2$$
$$+\frac{2}{3}(f-g-2h+j+k)^2.$$

......(10.26)

All other A(jj') are zero.

Then the intensity distribution of the second-order continuous spectrum is

$$(10.27)\quad I(\omega) = \tfrac{1}{2} I_0 \sum_{jj'} Z_{jj'}(\omega)\, C(j)\, C(j')\, A(jj') \left\{ \begin{array}{cc} \text{St.} & \text{A.St.} \\ 1 & e^{-\beta(j)-\beta(j')} \\ e^{-\beta(j')} & e^{-\beta(j)} \end{array} \right.$$

with A(jj'), C(j), and $\beta(j)$ taken at the point $\underline{q} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

## 11. NUMERICAL RESULTS.

### (a). First-order line spectrum.

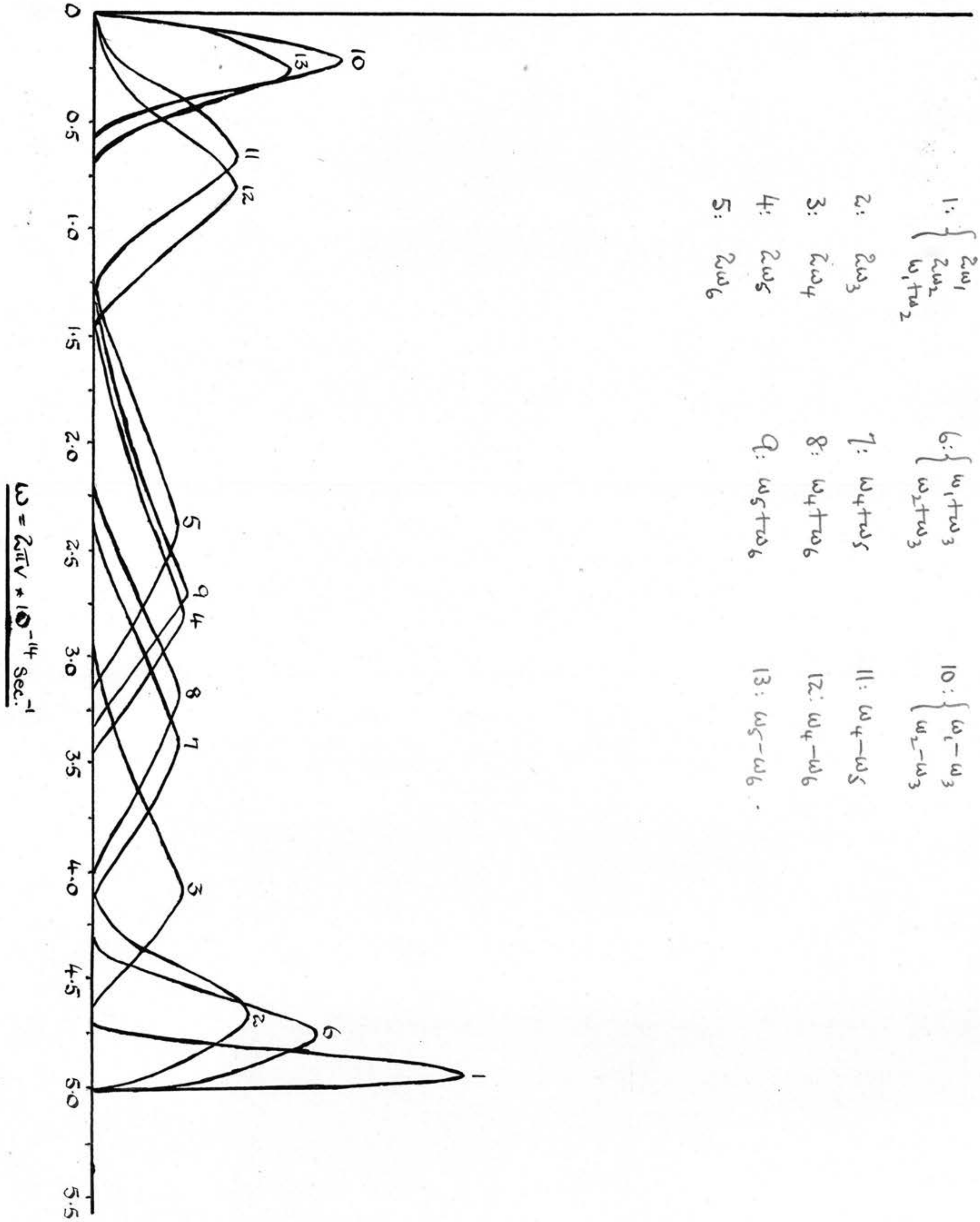
The observed value of the frequency shift of the principal Raman line (1332 $cm.^{-1}$) has already been used to determine the values of the atomic constants of the lattice (cf.(4.12)). The total intensity given by (10.12) contains as a factor the arbitrary constant $n = \alpha_{12,3}(1)$. The ratio of the intensity of the Stokes line to that of the anti-Stokes line is $e^{-\beta(1)}$ where $\beta(1) = \dfrac{\hbar\omega(1)}{kT}$.

Taking $\omega(1) = 2.51\times10^{14}$ $sec.^{-1}$, and the temperature of the crystal to be 300°K., this ratio is 586. The observed value given by Krishnan (1946c) is 575.

### (b). Second-order line spectrum.

The frequency shift of the single second-order Raman line of diamond is, from (10.20), twice the frequency shift of the first-order line, i.e. 2664 $cm.^{-1}$. This agrees satisfactorily with Krishnan's experimental result of 2666 $cm.^{-1}$. The intensity of this line (10.22) contains three arbitrary constants a,b,h. No data are available on the ratio of the intensities of the Stokes and anti-Stokes lines.

FIGURE 9.




FREQUENCY DENSITY FUNCTIONS $Z_{jj'}(\omega)$.

(c). Second-order continuous spectrum.

Referring to Section 4, the density functions $z_{jj'}(\omega)$ can be calculated from Table 7 by the same method that was used to obtain the frequency distributions. The range of values of $\omega$ is divided into equal intervals $d\omega = 0.6 \times 10^{14}$ sec.$^{-1}$ and then the number of combinations $\omega\binom{q}{jj'} = \omega\binom{q}{j} \pm \omega\binom{q}{j'}$ of frequencies belonging to the same wave-vector $\underline{q}$ can be counted in each interval. Three histograms are plotted, each shifted $0.2 \times 10^{14}$ sec.$^{-1}$ in the $\omega$ scale from the other two. These histograms are then smoothed out and give the frequency density curves $z_{jj'}(\omega)$.

From (10.26) we need consider only the 18 branches for which the A(jj') are not zero. The density functions $z_{jj'}(\omega)$ for these branches are shown in fig. 9, and the frequency shifts of the maxima of the branches are given in Table 12.

Table 12.

| | | | | | |
|---|---|---|---|---|---|
| 1: | $2\omega_1$<br>$2\omega_2$<br>$\omega_1+\omega_2$ | 2602 cm.$^{-1}$ | 7: | $\omega_4+\omega_5$ | 1805 cm.$^{-1}$ |
| 2: | $2\omega_3$ | 2469 " | 8: | $\omega_4+\omega_6$ | 1683 " |
| 3: | $2\omega_4$ | 2177 " | 9: | $\omega_5+\omega_6$ | 1434 " |
| 4: | $2\omega_5$ | 1487 " | 10: | $\omega_1-\omega_3$<br>$\omega_2-\omega_3$ | 106 " |
| 5: | $2\omega_6$ | 1258 " | 11: | $\omega_4-\omega_5$ | 345 " |
| 6: | $\omega_1+\omega_3$<br>$\omega_2+\omega_3$ | 2522 " | 12: | $\omega_4-\omega_6$ | 409 " |
| | | | 13: | $\omega_5-\omega_6$ | 133 " |

Comparison of fig. 9 with Krishnan's experimental results shows that the factors $A(jj')$ must be zero for the branches 4,5,7,8,9,11,12,13; i.e.

$$(11.1) \qquad A(55) = A(66) = A(45) = A(46) = A(56) = 0.$$

The branches (10) $\{(\omega_1-\omega_3)$ and $(\omega_2-\omega_3)\}$ may be covered by the incident mercury line. Further the calculated maxima at 2177 cm.$^{-1}$ and 2469 cm.$^{-1}$ can be identified with the experimental peaks at 2176 cm.$^{-1}$ and 2460 cm.$^{-1}$. These calculated frequency shifts depend only on the measured elastic constants, the lattice constant, and the frequency shift of the principal Raman line. Krishnan claims to identify a number of additional peaks on either side of the main maximum at 2460 cm.$^{-1}$, but from the microphotometer record, there is no reason to suppose that these are anything other than random fluctuations of intensity.

Now from (10.26), if $A(55) = 0$,

$$(11.2) \qquad \begin{cases} a + b = c + e, \\ \quad b = d, \\ f + g = j + k, \\ \quad f = h, \end{cases}$$

and so $\qquad A(66) = A(56) = 0.$

If $A(45) = A(46) = 0$, then using (11.2),

$$a = c \; : \; b = d = e : \; f = h = j \; : \; g = k : \quad \text{i.e.}$$

$$
(11.3) \quad \begin{cases}
\alpha_{11,11}(1) = \alpha_{11,12}(1), \\
\alpha_{11,22}(1) = \alpha_{11,23}(1) = \alpha_{11,33}(1) = \alpha_{11,31}(1), \\
\alpha_{12,11}(1) = \alpha_{12,12}(1) = \alpha_{12,22}(1) = \alpha_{12,23}(1), \\
\alpha_{12,33}(1) = \alpha_{12,31}(1).
\end{cases}
$$

Then the remaining non-zero A(jj') become

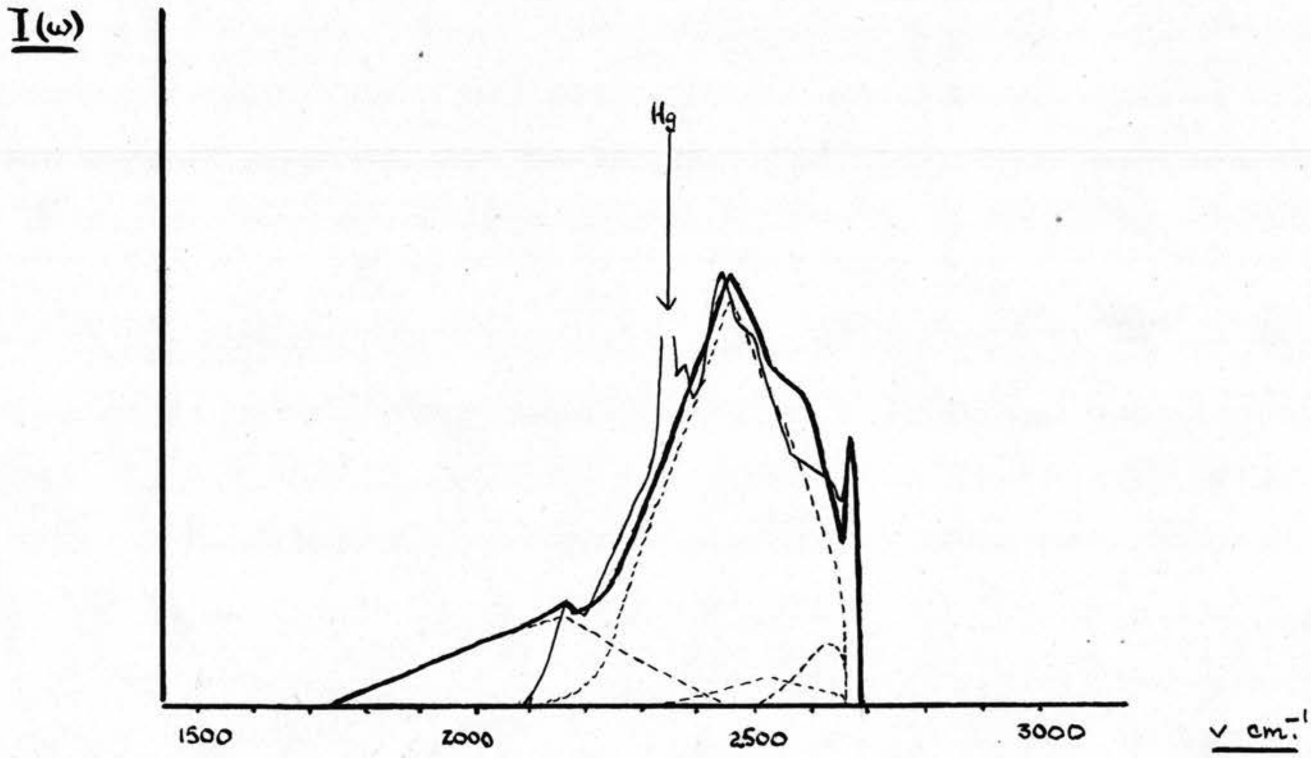
$$
(11.4) \quad \begin{cases}
A(11) = A(22) \\
\qquad = \frac{32}{3m^2}\left[a^2 + 2ab + 3b^2 + 6f^2\right], \\
A(33) = \frac{4}{m^2}\left[\frac{1}{9}(a+2b)^2 + 3\left(\frac{2}{3}f - g\right)^2\right], \\
A(44) = \frac{4}{m^2}\left[(a+2b)^2 + 3(2f+g)^2\right], \\
A(12) = \frac{32}{3m^2}\left[\frac{1}{3}(a-b)^2 + 4f^2\right], \\
A(13) = A(23) \\
\qquad = \frac{4}{3m^2}\left[\frac{1}{3}(a-b)^2 + (f+3g)^2\right].
\end{cases}
$$

Table 13 gives the values of $e^{-\beta(j)}$ and C(j) for the point $\underset{\sim}{q} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, taking the temperature of diamond to be 300°K..

Table 13.

| $j$ | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| $\omega_j \times 10^{-14}$ | 2.50 | 2.50 | 2.34 | 2.11 |
| $e^{-\beta(j)}$ | 0.00175 | 0.00175 | 0.00263 | 0.00470 |
| $\frac{2C(j)}{\hbar} \times 10^{14}$ | 0.401 | 0.401 | 0.429 | 0.476 |

FIGURE 10.




(Stokes branches.)

Fine line is sketch of Krishnan's microphotometric record of the Raman spectrum of **diamond** (Krishnan (1946 c)): broken lines represent theoretical contributions to the intensity of frequency density functions $z_{jj'}(\omega)$ after multiplication by appropriate factors: thick line represents the superposition of these functions, i.e. the total theoretical intensity.

The frequency density functions corresponding to the non-zero $A(jj')$ are then multiplied by products and squares of these $C(j)$ and $e^{-\beta(j)}$ as in (10.27). Lastly, by choosing appropriate values of ratios of the $A(jj')$ in (11.4) it is possible to approximate to the observed total intensity of the Stokes branches; the final result is shown in fig. 10 below, which contains the separate branches, the total intensity, and Krishnan's experimental curve. The ratios between the $A(jj')$ are

$$(11.5)\quad \left\{ \begin{aligned} &A(33) : A(44) : A(11) : A(13) \\ &\qquad = 40 : 12 : 1 : 1. \end{aligned} \right.$$

From the relations (11.3), (11.4) and (11.5) between the derivatives of the polarisability tensor, it may be possible to obtain information about the electronic configurations in the two types of diamond.

The approximation could be improved by removing the degeneracies in the frequency spectrum, by considering elements of the polarisability tensor referring to second neighbour atoms, or by calculating the eigen-vectors for more than one point in reciprocal space. The agreement between experiment and theory is, however, sufficient to show that lattice dynamics is able to give a satisfactory explanation of the Raman spectrum of diamond.

I wish to thank Professor M. Born, who suggested this problem to me, for his continued interest and his advice on many occasions.

REFERENCES.


Adams 1921 Journ. Wash. Acad. Sci., 11, 45.

Aitken 1937 Proc. Roy. Soc. Edin., 57, 269.

Bhagavantam & Bhimasenachar 1944 Nature, 154, 546.

" " " 1946 Proc. Roy. Soc. A, 187, 381.

Blackman 1937 Proc. Roy. Soc. A, 159, 416.

Born 1914 Ann. Phys. Leipzig, 44, 605.

" 1923 Atomtheorie des Festen Zustandes, Leipzig.

" 1940 Proc. Camb. Phil. Soc., 36, 160.

" 1942 Reports on Progress in Physics, 9, 294.

" 1946 Nature, 157, 582.

Born & Begbie 1947 Proc. Roy. Soc. A, 188, 179.

Born & Bradburn 1947 Proc. Roy. Soc. A, 188, 161.

Born & v. Karman 1912 Phys. Z., 13, 297.

Bragg & Bragg 1913 Proc. Roy. Soc. A, 89, 277.

Hopf & Lechner 1914 Verh. deutsch. Phys. Ges., 16, 643.

Krishnan 1944 Proc. Ind. Acad. Sci., 19, 216.

" 1946a Proc. Ind. Acad. Sci., 24, 33.

" 1946b " " " " , 24, 45.

" 1946c " " " " , 24, 25.

Landolt-Börnstein 1927 Phys.-Chem. Tabellen, Berlin.

Magnus & Hodler 1926 Ann. Phys. Leipzig, 80, 808.

Nagendra Nath 1934 Proc. Ind. Acad. Sci., 1, 333.

Nernst 1911 Ann. Phys. Leipzig, 36, 395.

Pitzer 1938 J. Chem. Phys., 6, 68.

Placzek 1934 Handbuch der Radiologie, ed. Marx, 6, pt. 2.

Raman 1941 Proc. Ind. Acad. Sci., 14, 459.

" 1944 " " " " , 19, 189.

Robertson, Fox & Martin 1934 Phil. Trans. Roy. Soc., 232, 463.

" " " " 1936 Proc. Roy. Soc. A, 157, 579.

Sommerfeld & Bethe 1933 Handbuch der Physik, 24, pt.2, 402.

Williamson 1922 Journ. Frank. Inst., 193, 491.